

**Master Thesis**

# **Experimental determination of single bubble behavior in a high-pressure optical alkaline electrolyzer**

**Pablo Estruga**

Matriculation Number: 1991964

Examiner: Prof. Dr.-Ing. Thomas Schulenberg  
Dra.-Ing. Cecilia Smoglie

Tutor: Dr. Ing. Thomas Jordan

Karlsruhe, 26. Jun. 2017

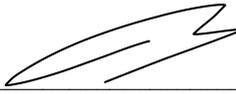


## Declaration of Authorship

I declare that I have developed and written the enclosed Master Thesis completely by myself, and have not used sources or means without declaration in the text. Any thoughts from others or literal quotations are clearly marked. The Master Thesis was not used in the same or in a similar version to achieve an academic grading or is being published elsewhere.

Karlsruhe, 26.06.2017

Place, Date

A stylized, handwritten signature consisting of several overlapping, curved lines that form a shape resembling a leaf or a calligraphic flourish.

Signature



# Abstract

## English

The participation of renewable energy in the energetic matrix is increasing continuously and the electrical energy storage technologies will be crucial in the future energy sector scenario. With this technologies, it is possible to regulate the fluctuating electrical energy generation that renewable energy sources present. Under the “Power to gas” concept, hydrogen can be generated with the surplus of those sources (e.g. solar and wind power). Thus, it is essential to increase the efficiency of the storage technologies. The generation of hydrogen by means of high pressure electrolysis is presented as a possible solution [1].

This master thesis was done within the cooperation program between the Institute of Nuclear and Energy Technologies (IKET) and the Instituto Tecnológico de Buenos Aires (ITBA). Experiments were performed with an alkaline high-pressure experimental electrolyzer, where pressure was rise up to 180bar. It was studied the case of single bubbles behavior, focusing on the typical diameters and rise velocities of hydrogen and oxygen bubbles. The obtained results were compared with a bubbles swarm behavior, where clear differences were observed. To achieve the single bubble generation, a new electrode was design and an electrical pulsed signals was applied as power supply.

## Deutsch

Der Anteil von erneuerbaren Energien am globalen Energiemix wächst kontinuierlich und die Elektrizitätsspeichertechnologien werden im Energiesektor in der Zukunft eine entscheidende Rolle spielen. Mit solchen speichern ist es möglich die schwankende Produktion der elektrischen Energie zu regulieren, die aus den erneuerbaren Energiequellen stammt. Mit dem Konzept “Power to gas” wird Wasserstoff mit Hilfe der Überflüsse an Solar- und Windenergie produziert. Entscheidend die Effizienz der Speichertechnologien weiter zu erhöhen. Die Wasserstoffherstellung durch Hochdruckelektrolyse wird dabei als ein möglicher Ansatz präsentiert [1].

Diese Masterarbeit entstand im Rahmen des Kooperationsprogramms des Instituts für Kern- und Energie Technologie (IKET) am KIT und des Instituto Tecnológico de Buenos Aires (ITBA). Die Versuche wurden mit einem alkalischen Hochdruck-Elektrolyseur mit einem Arbeitsdruck bis 180bar durchgeführt. Es wurde dabei das Verhalten einzelner Blasen untersucht. Der Fokus lag auf den typischen Durchmesser und der Aufstiegsgeschwindigkeiten der Wasserstoff- und Sauerstoffbläschen. Um die Produktion einer einzelnen Blase sicherzustellen, wurde eine neue Elektrode entworfen und ein neues elektrisches Pulssignal zur Stromversorgung verwandt. Die so erhaltenen Resultate wurden mit den Blasenschwarm Verhalten verglichen, wobei deutliche Unterschiede beobachtet wurden.

## Español

A nivel mundial crece la participación de energía renovable en la matriz energética. Las tecnologías de almacenamiento de energía eléctrica serán cruciales en los futuros escenarios del sector energético. Estas tecnologías permiten regular la fluctuante generación de energía eléctrica generada a partir de fuentes renovables. Bajo el concepto “Power to gas”, se puede obtener hidrogeno con el excedente de energía proveniente de estas fuentes de energía (p.ej. Energía solar y eólica). Por lo tanto, es imprescindible que las técnicas de almacenamiento sean cada vez más eficientes. La generación de hidrogeno mediante electrólisis a alta presión se presenta como posible solución [1].

En este trabajo de tesis que se realizó dentro del convenio de cooperación entre el Institut of Nuclear and Energy Technologies (IKET) y el Instituto Tecnológico de Buenos Aires (ITBA). Se realizaron experimentos con un electrolizador experimental alcalino de alta presión, donde se aumentó la presión hasta los

180bar. Se estudió el comportamiento de las burbujas de hidrógeno y oxígeno generadas de manera individual. El foco fue puesto en el diámetro característico y la velocidad de ascenso las burbujas. Los resultados se compararon con el comportamiento que presentan múltiples burbujas, donde se han observado claras diferencias. Para lograr obtener una generación singular de burbujas, se diseñó un nuevo electrodo y como fuente de energía se utilizó una señal eléctrica pulsante.





# Content

<b>Abstract</b> .....	<b>i</b>
<b>Content</b> .....	<b>v</b>
<b>List of figures</b> .....	<b>ix</b>
<b>1 Introduction</b> .....	<b>13</b>
1.1 Objective .....	13
1.2 Scope.....	14
<b>2 Theoretical Background</b> .....	<b>15</b>
2.1 Water Electrolysis .....	15
2.1.1 Chemical and thermodynamic process.....	15
2.1.2 High pressure electrolysis .....	16
2.2 Bubble Behavior.....	17
2.2.1 Nucleation.....	17
2.2.2 Growth .....	18
2.2.3 Detachment .....	18
2.2.4 Rise .....	19
2.2.5 Bursting.....	19
<b>3 Electrolyzer</b> .....	<b>21</b>
3.1 Original configuration.....	21
3.2 New configuration and new electrodes .....	23
3.2.1 New Electrodes .....	23
3.2.2 New Electrolyzer set up .....	24
<b>4 Equipment</b> .....	<b>27</b>
4.1 Electrolyzer .....	27
4.2 Power Supply .....	27
4.3 Optical equipment .....	28
4.3.1 Laser .....	28
4.3.2 Camera .....	29
4.3.3 Microscope.....	29
4.3.4 Calibration .....	29
4.3.5 Taking Images.....	30
<b>5 Safety Analysis</b> .....	<b>31</b>
5.1 Potassium Hydroxide Solution.....	31
5.2 Cleaning and Maintenance .....	31
5.3 Modifications .....	33
5.3.1 Container.....	33
5.3.2 Gas Valve.....	33
5.3.3 Exhaust Valve .....	34
5.4 Hydrogen Production .....	34
<b>6 Experimental Measurements and Parameters</b> .....	<b>35</b>
6.1 Experimental Set-Up .....	35

6.2	Parameters .....	36
6.2.1	Power Supply .....	36
6.2.2	Working Pressures .....	36
6.2.3	Potassium Hydroxide Solution.....	36
6.3	Optical measurements .....	36
6.3.1	Images .....	36
6.3.2	Processing the images .....	36
6.3.3	Analyzing the images.....	38
6.4	Error .....	40
<b>7</b>	<b>Results .....</b>	<b>41</b>
7.1	Bubbles size.....	41
7.1.1	Atmospheric pressure.....	41
7.1.2	High pressure .....	49
7.2	Rising Velocity.....	54
7.2.1	Atmospheric Pressure.....	54
7.2.2	High Pressure .....	60
7.3	Life time at free surface.....	65
7.3.1	Hydrogen.....	65
7.3.2	Oxygen.....	68
<b>8</b>	<b>Summary .....</b>	<b>71</b>
<b>9</b>	<b>References .....</b>	<b>73</b>





# List of figures

Figure 2.1: Acting forces on a bubble attached to a horizontal electrode. Zhang, 2012. [9] .....	18
Figure 2.2: Bursting of a bubble and its excess pressure. S.D. Lubetkin, 1995 [8]. .....	19
Figure 3.1: High-pressure electrolyzer scheme. Frey. [4].....	21
Figure 3.2: Optical Chamber.....	21
Figure 3.3: High-pressure electrolyzer – Original configuration. ....	22
Figure 3.4: New glass coated wire electrodes. ....	23
Figure 3.5: New electrode. Finished model. ....	23
Figure 3.6: Optical chamber inputs, old configuration. ....	24
Figure 3.7: Optical chamber, electrodes new configuration. ....	24
Figure 3.8: Optical chamber inputs, new configuration. 3: Plug - 4: draining - 5: Glassed electrode .....	25
Figure 3.9: Electrolyzer Scheme, new configuration.....	25
Figure 3.10: New electrode for single bubble generation with pulsed signal. ....	26
Figure 4.1: Electrical Circuit.....	27
Figure 4.2: Optical beam path scheme. LaVision, 2016 [18]. ....	28
Figure 4.3: Taken Image of the scaling plate.....	29
Figure 4.4: Electrolyzer, laser and camera scheme. F. Frey, 2016 [4].....	30
Figure 4.5: Consecutive images taken by laser cameras 1 and 2 with a time delay of 11000 $\mu$ s.....	30
Figure 5.1: Electrolyzer surface - (a) Hole for electrode. (b), (c) Solution Valve. ....	31
Figure 5.2: Optical chamber – (d) Lens. (e), (f) Vessel interior. ....	32
Figure 5.3: Electrolyzer after being cleaned – (a) Device. (b) Optical chamber.....	32
Figure 5.4: Metal sheet container.....	33
Figure 5.5: Optical chamber, pressure valves and gauge – New connection. ....	33
Figure 6.1: Experimental Set up. ....	35
Figure 6.2: Liner object at image scale bar.....	37
Figure 6.3: IMAGE J threshold interface.....	37
Figure 6.4: Image processing.....	37
Figure 6.5: Results of analyzed particles by IMAGE J.....	38
Figure 6.6: Vertical configuration.....	39
Figure 7.1: H <sub>2</sub> diameter distribution – 1.5 Volts, Period 450ms, Pulse time 50ms – 1 bar.....	41
Figure 7.2: H <sub>2</sub> diameter distribution – 1.6 Volts, Period 510ms, Pulse time 10ms – 1 bar .....	42
Figure 7.3: H <sub>2</sub> diameter distribution – 1.7 Volts, Period 210ms, Pulse time 10ms – 1 bar .....	42
Figure 7.4: H <sub>2</sub> diameter distribution – 1.8 Volts, Period 510ms, Pulse time 10ms – 1 bar .....	42
Figure 7.5: H <sub>2</sub> diameter distribution – 1.9 Volts, Period 710ms, Pulse time 10ms – 1 bar .....	43
Figure 7.6: Analysis of the images, reference and new bubbles in consecutive pictures .....	44
Figure 7.7: Single hydrogen bubble diameter per pulse vs. applied voltage.....	45
Figure 7.8: O <sub>2</sub> diameter distribution – 1.5 Volts, Period 450ms, Pulse time 50ms – 1 bar .....	45
Figure 7.9: O <sub>2</sub> diameter distribution – 1.6 Volts, Period 510ms, Pulse time 10ms – 1 bar. ....	46

Figure 7.10: O <sub>2</sub> diameter distribution – 1.7 Volts, Period 210ms, Pulse time 10ms – 1 bar.....	46
Figure 7.11: O <sub>2</sub> diameter distribution – 1.8 Volts, Period 510ms, Pulse time 10ms – 1 bar.....	46
Figure 7.12: O <sub>2</sub> diameter distribution – 1.9 Volts, Period 710ms, Pulse time 10ms – 1 bar.....	47
Figure 7.13: Diameter of one oxygen bubble per pulse vs. applied voltage. ....	48
Figure 7.14: Hydrogen and Oxygen moles production vs. applied voltage. ....	49
Figure 7.15: Hydrogen bubble diameter distribution – 1bar, 40bar, 180bar.....	50
Figure 7.16: Hydrogen - Diameter as function of pressure.....	51
Figure 7.17: Oxygen bubble diameter distribution .....	52
Figure 7.18: Oxygen - Diameter as function of pressure .....	53
Figure 7.19: H <sub>2</sub> bubble rising velocity distribution – 1,7V – 1bar.....	54
Figure 7.20: H <sub>2</sub> bubble rising velocity distribution – 1,9V – 1bar.....	55
Figure 7.21: H <sub>2</sub> Data set and tendency lines of the rising vel. as function of vertical position of bubbles with diameters of 59µm and 74µm – 1.7V – 1bar.....	56
Figure 7.22:H <sub>2</sub> Data set and tendency lines of the rising vel. as function of vertical position of bubbles with diameters of 36µm and 92µm – 1.9V – 1bar.....	56
Figure 7.23: Hydrogen rising velocity average per diameter – All applied voltages – 1 bar. ....	57
Figure 7.24: Oxygen rising velocity distribution – 1,7V – 1bar.....	58
Figure 7.25: Oxygen rising velocity distribution – 1,9V – 1bar.....	58
Figure 7.26: Figure 1.22: Data set and tendency lines of the rising vel. as function of vertical position for oxygen bubbles with diameters of 92µm and 102µm – 1.7V – 1bar.....	59
Figure 7.27: Data set and tendency lines of the rising vel. as function of vertical position for oxygen bubbles with diameters of 59µm and 61µm – 1.9V – 1bar. ....	59
Figure 7.28: Oxygen rising velocity average per diameter – 1 bar. ....	60
Figure 7.29: Oxygen and Hydrogen rising velocity distribution.....	60
Figure 7.30: Hydrogen rising velocity as function of pressure 1,7V – 10ms time pulse – 1010ms period	61
Figure 7.31: Oxygen rising velocity as function of pressure.....	62
Figure 7.32: Hydrogen and oxygen bubble terminal velocities.....	62
Figure 7.33: Hydrogen and Oxygen rising velocity as function of diameter. Comparison between previous and actual results.....	64
Figure 7.34: Sequence of 99µm diameter hydrogen bubble at the free surface .....	65
Figure 7.35: Lifetime of bubbles as function of diameter. ....	66
Figure 7.36: Bursting of 140µm diameter hydrogen bubble .....	66
Figure 7.37: Bursting of 180µm and 110µm diameter hydrogen bubbles.....	67
Figure 7.38: Bursting several hydrogen bubbles.....	67
Figure 7.39: Bursting several hydrogen bubbles.....	67
Figure 7.40: Bursting of a 270µm oxygen bubble.....	68
Figure 7.41: Oxygen bubble of 237µm going through the free surface .....	68
Figure 7.42: Oxygen bubble rises and bursts. Diameter could not be measured.....	69
Figure 7.43: Oxygen bubble of 245µm diameter rises stays at free surface and bursts. ....	69





# 1 Introduction

In Argentina, Law 27.191 establish that 8% of generated energy must be obtained from renewable sources by 2017 and 20% by 2025 [2]. In Germany, the Energiewende defines the consumption of energy that must come from renewable energy: 35% (2020), 50% (2030), 65% (2040), and 80% (2050) [3].

When the new energy sector scenario is analyzed, storage technologies plays a key role. These technologies can balance the energy generation from renewable, which are known to be characterized by their fluctuating behavior. Electrolyzers present a way of transforming electrical energy in the chemical bonds of hydrogen, under the concept known as "power-to-gas". By electrolysis, water molecule is split in hydrogen and oxygen, which are then stored. This energy can be again obtained by the reverse chemical reaction in a fuel cell or by combustion in a combustion engine.

Besides the balancing of grid function, hydrogen is required as a product in the chemical industry and mobility sector. Actually, the worldwide production is around 600billion Nm<sup>3</sup>/year [1], amount that is being produced from hydrocarbons. Then, if hydrogen would be obtained by electrolysis supplied by renewable energies, the contribution to the reduction of CO<sub>2</sub> would be much more than considerable and the hydrogen CO<sub>2</sub> footprint would be reduced.

Moreover, conventional electrolysis process can be improved; high-pressure electrolyzers compress the liquid in a previous step generating compressed hydrogen and oxygen. The compression of the water requires less work than the compression of the gas from atmospheric pressure. However, the gas generation at high pressures presents some difficulties, like the increment of diffusive losses of the gases. Another problem is the proper transport of the bubbles through and separation from the electrolyte.

In order to study and characterize the gas bubbles behavior at high pressure, the Institute for Nuclear and Energy Technologies (IKET) and the Instituto Tecnológico de Buenos Aires are cooperating on the project of an experimental high-pressure optical electrolyzer. In a previous work, Frey has shown their results regarding the size and rising velocity of the bubbles [4]. However, measurements were difficult to be taken due to the bubble swarm generation.

In this master thesis single bubbles are studied, the differences between both behaviors, swarm and single bubble production, is analyzed.

## 1.1 Objective

The aim of this master thesis is to obtain experimental data from optical measurements in order to investigate:

- Bubble detachment diameter and its relation with the working pressure, range from ambient pressure up to 180bar.
- The bubble rising velocity depending on the bubble diameter.
- The lifetime of the bubbles at the free surface.

These experiments were performed under different power supply input. The influence of different applied currents and voltages on the mentioned points is also part of these studies.

Avoiding bubble swarm formation is other objective of this thesis; therefore, new electrodes had to be developed with reduced surface in comparison with previous models.

In addition, a safety analysis was performed, focusing on the equipment operation, hydrogen production and its flammability limits, known and general safety rules and good conduct behavior while working in the laboratory.

Finally, the analysis of the data, results and conclusions are presented in this document.

## **1.2 Scope**

The master thesis includes the realizations of the experiments, data collection, analysis and interpretation of the results and conclusion. In this document, the whole work is described as well as the analysis and results with their respective conclusion.

The experiments were performed with the high-pressure electrolyzer at IKET laboratory.

# 2 Theoretical Background

## 2.1 Water Electrolysis

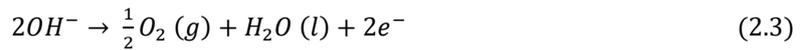
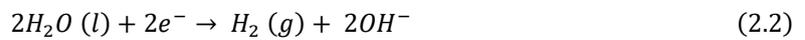
The water electrolysis is an electrochemical process where an electrical current splits the water molecule into its components hydrogen and oxygen. Usually direct current is supply, however, other electrical signals, as pulses, can be applied. Thus, the electrolyzer transforms electrical energy into chemical energy stored in hydrogen and oxygen.

Briefly, in order to produce a current circulation, voltage is applied on a pair of electrodes, with the anode positively charged and the cathode negatively charged. To close the circuit, both electrodes are immersed into an electrolyte, which typically is acidic or caustic, contributing with a high concentration of ions ( $OH^-$ ,  $H^+$ ) to increase the conductivity. To avoid the mixing of generated gases, electrodes are separated by a membrane, which is permeable to ions. Actually, membranes are also permeable to gases, especially to hydrogen because of its high diffusivity. Electrolysis has its inverse process where chemical energy is converted into electrical energy. A fuel cell is used for this purpose, where the stored hydrogen and oxygen combine, forming water and producing electricity.

Industrial electrolyzers are well established with operating temperatures between 70–90°C, cell voltage of 1.85–2.05V and current densities of 2 to 3kA/m<sup>2</sup>. The energy consumption is 4–4.5kWh/Nm<sup>3</sup>H<sub>2</sub>, corresponding to efficiencies of about 80%. Under these conditions 2MW are required to generate approximately 500Nm<sup>3</sup> of hydrogen per hour, for instance. With regard to purity of the produced gases, 99.9% for hydrogen and 99.8% for oxygen is achieved [1].

### 2.1.1 Chemical and thermodynamic process

For the investigations of high-pressure electrolysis, alkaline water electrolysis has been selected. Potassium hydroxide solution was used as electrolyte. The process is governed by the chemical equation (2.1), which shows the splitting of the molecule of water. The chemical reactions at the electrodes are presented as well in equations (2.2) for the cathode and (2.3) for the anode.



The exothermal reaction (2.4) that gives water as a product, by means of combustion or a fuel cell e.g., can be characterized by the enthalpy of formation  $-\Delta H$ , that by definition can be written as in equation (2.5), where  $-\Delta G$  is the Gibbs energy and  $-T\Delta S$  is heat:



$$-\Delta H(t, p) = -\Delta G(t, p) - T\Delta S(t, p) \quad (2.5)$$

The Gibbs energy may be converted into electricity, while the losses associated with the entropy are converted into heat. For the irreversible electrolysis, both energies have to be provided from electricity. Thus, the voltage needed is:

$$V_{th} = \frac{\Delta G(t, p) + T\Delta S(t, p)}{nF} = 1.48V \quad (2.7)$$

Where  $n$  is the number of electrons, in this case they are two, and  $F$  the Faraday constant. As this functions are dependent on temperature and pressure the next step would be to analyze what happens with the electrolysis when is performed under high pressures.

## 2.1.2 High pressure electrolysis

Electrolysis is a key process to obtain carbon-free hydrogen- Therefore, it is important to improve the electrolyzer efficiency. Moreover, it is a necessity to improve not only the electrolysis stage, but also the whole process, as for example the gases capture and pressurization, then, the working pressure is a parameter to be taken into account.

The increasing of the electrolyte pressure reduces the gas bubbles size. Therefore, the ohmic resistance, due to the attached bubbles at the electrodes, is reduced leading to a less power consumption [5].

Moreover, K. Onda [6] has estimated the voltage electrolysis for different temperatures and pressures, basing his calculation on LeRoy et al work [7]. Basically, the needed voltage decreases with increasing temperatures and increases with increasing pressures, however, the increase was found to be small for pressures above  $20\text{Mpa}$ . The higher efficiency is related to the included compression process. The production of hydrogen under high pressure requires less energy than its generation at ambient pressure and its later compression. For pressurizing the system water is previously compressed, which requires less energy than the compression of a gas. As a result, the ideal pressure and temperature for water electrolysis were obtain, being  $70\text{Mpa}$  and  $250^\circ\text{C}$  correspondingly [6]. Table 2.1 shows the energy consumption by the pumps and compressors.

Table 2.1: Change of hydrogen production by pressure. K.Onda, 2004 [6]

$p$ (MPa)	$W_{\text{pump}} + W_{\text{ele},298,p}$ (kW)	$W_{\text{ele},298,0.1} + W_{\text{comp}}$ (kW)
0.101325	237.2	237.2
10	254.5 (0.36)	264.2 [27.0]
22.064	257.8 (0.80)	269.9 [32.6]
40	260.6 (1.45)	274.3 [37.1]
70	263.8 (2.53)	278.7 [41.5]

Values in ( ) represent water pump power at  $\eta = 50\%$ ; and in [ ], hydrogen compressor power at  $\eta = 50\%$ .

Table 2.1 shows a short summary of the conclusions obtained by K. Onda, whom results showed that the power needed for the production of hydrogen under high pressure is approximately 5% less than the power required for atmospheric water electrolysis and later compression of the hydrogen. Compressor and pump efficiencies are assumed to be 50% [6].

## 2.2 Bubble Behavior

Studying the bubble behavior is of utmost importance because, and in agreement with Lubetkin [8], they influence the efficiency of the electrolysis process, which is not only of technical but also of economic interest. In order to gain efficiency, the resistance at the electrodes should be minimized. The electrolytic gas bubbles provide a major contribution to the resistance [9].

Following Lubetkin work, bubbles have different stages in which are developed: Nucleation, growth, detachment, rise and bursting [8]. Moreover, from these five stages, Zhang and Zeng mention the first three as the ones that strongly influence the resistance value, as they defined the residence time and diameter of the gas bubbles [9].

The same three stages involved in the bubble formation are also mentioned by Sequeira [10]. In his words, a short description of the bubble formation process is described: *“The physics of gas evolution proceeds through three phases: nucleation, growth and detachment. Bubbles start nucleating at electrode surface from solution once the solution becomes highly supersaturated with produced gas. Subsequently, bubbles grow by dissolved gas diffusion to their surface or by coalescence with other bubbles, and finally detach from the electrode when the forces pulling them away overcome the surface forces binding them”*.

### 2.2.1 Nucleation

As it was mentioned before, and following Sequeira [10], after short time the electrolyte close at the electrode will be supersaturated of gas. As hydrogen is barely soluble, just a current density of a few milliamperes per square centimeters is needed to supersaturate the liquid. When the concentration of the dissolved gases exceed a critical point, bubbles start to nucleate. The classical nucleation theory defines the critical radius, which determines if the vapor nuclei would grow or decay depending on whether the bubble nucleus is higher or smaller than the critical radius value. At this point, the bubble is in a chemical and mechanical metastable equilibrium with the surroundings. The key points of the nucleation theory are the expressions that define the critical bubble nucleus size and the nucleation frequency [10]. Equation 2.8 shows the expression for the critical radius obtained by Ward [11]:

$$R_c = \frac{2\sigma}{\frac{\eta P_\infty}{v_1} + \frac{P' C'}{v_2 C_0} - P'} \quad (2.8)$$

Where  $P_\infty$  is the vapor pressure of solvent at the temperature of the liquid;  $P'$  is the external pressure in the liquid;  $v_1$  and  $v_2$  are the vapor phase activity coefficients of the solvent and solute;  $C'$  is the concentration of the gas in the solution surrounding the bubble, expressed as moles of solute per mole of solvent;  $C_0$  is the equilibrium concentration of the gas in the solvent when a flat surface of the solvent is exposed to the gas only at  $T'$  and  $P'$ , expressed as moles of solute per mole of solvent;  $\sigma$  is the surface tension of the liquid-gas interface often assumed equal to the surface tension of the liquid vapor interface.

$\eta$  is defined as:

$$\eta = \exp\left(\frac{V_1(P' - P_\infty)}{kT}\right) \quad (2.9)$$

Where  $V_1$  is the specific volume of the pure solvent. The nucleation rate  $J$  ( $s/cm^3$ )<sup>-1</sup>, is also derived from the nucleation theory. Lubetkin provides the following definition [12]:

$$J = C \exp\left(\frac{-\Delta G}{kT}\right) \quad (2.10)$$

Where  $C$  is a constant known as the frequency factor,  $\Delta G$  the free energy needed to be overcome,  $k$  the Boltzman constant and  $T$  the temperature.

### 2.2.2 Growth

At this stage, bubbles increase their size due to diffusion of gas towards the gas – liquid interface and coalescence of bubbles. Sides [13] gives a description of the process, which first presents coalescence of bubbles, followed by diffusion. The growth of the bubble, which depends on how rapidly diffusion occurs across the interface, can be characterized by the time dependence of the radius. Scrivens [14] derived an expression for single bubbles radius showed in equation (2.11):

$$R(t) = 2\beta(\Delta t)^{1/2} \quad (2.11)$$

Where  $\beta$  is a constant which depends on the supersaturation conditions.

### 2.2.3 Detachment

At this stage, bubbles detach from electrode surface. This happens once the surface adhesive forces, depending on the bubble contact angles, no longer restrain them [15]. Following Zhang analysis, forces are arranged in the  $x$  and  $y$  direction, their balance will determine if the bubble stays attached to the electrode. The forces that come into play are the buoyancy,  $F_B$ , due to the density differences between the liquid and the gas; the expansion force,  $F_G$ , due the growth of the bubble its pressure experiences a dynamic change; the surface tension force,  $F_S$ , acting along the circular contact area where the gas, liquid and solid phases are in contact with each other and the drag force,  $F_D$ , due to the interaction of the bubble in a viscous medium [9]. Figure 2.1 shows the forces acting on a bubble.

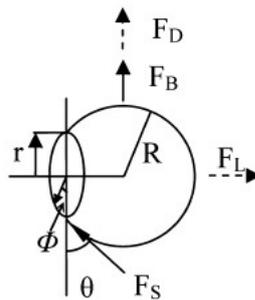


Figure 2.1: Acting forces on a bubble attached to a horizontal electrode. Zhang, 2012. [9]

Moreover, and in concordance with Zhang, Lubetkin [8] presents the same forces and mentions two more that may be included, as in this case bubbles are generated by electrolysis. This forces are the Marangoni force,  $F_M$ , resulting from a gradient of the surface tension, and the electrostatic interaction force,  $F_E$ , between the bubble and the solid surface of the electrode. The Marangoni effect will always try to retain the bubble, helping to increase the bubble diameter at the detachment, while the electrostatic force may either

reduce or increase the detachment diameter, depending on if the bubble shares the charge, or has the opposite, of the electrode correspondingly. This forces may have influence at the rising stage, when the bubble is still in the nearby of the electrode.

Finally, the bubble detaches when the equilibrium is broken, the diameter of the detached bubble that is measured, is considered to be the same as detached diameter at the moment where the disequilibrium occurs. Moreover, the orientation and shape of the electrodes are consider to have an effect on the bubble size [16], as this parameters influence the acting forces.

## 2.2.4 Rise

At this stage, the bubble rises with a certain velocity though the electrolyte solution until it reaches the free surface. This behavior can be understood by applying the Navier-Stokes equation (2.12). Furthermore, the Stokes law, which predicts a limit velocity, is one of the possible solution (2.13).

$$\rho \frac{Du}{Dt} = \rho g - \nabla p + \mu \nabla^2 u \quad (2.12)$$

$$U_l = 2gr^2\Delta\rho/9\mu \quad (2.13)$$

Where  $p$  is the pressure,  $\Delta\rho$  is the density difference between the liquid and gaseous phases,  $r$  is the diameter of a spherical bubble of equivalent volume,  $\mu$  is the dynamic viscosity of the liquid and  $g$  is the acceleration of gravity. The main hypothesis is that the bubble is a solid sphere and it does not change its size during the rising, what was comply in these studies.

In addition, the bubble accelerates from the electrode until it reaches the terminal velocity. At the beginning of the rising, bubble may be affected also by the already mentioned Marangoni effect and the electrostatic force, as they influence the bubble in the vicinity of electrode [8]. After analyzing the images, acceleration effect on the bubble was detected.

## 2.2.5 Bursting

Bursting is the last stage of the process, here the bubble reaches the liquid free surface staying some time at this point, foam can be generated. Then, the bubble passes through the free surface into the gas phase. Figure 2.2 shows the scheme of the process and the internal pressures of the bubble and soap bubble.

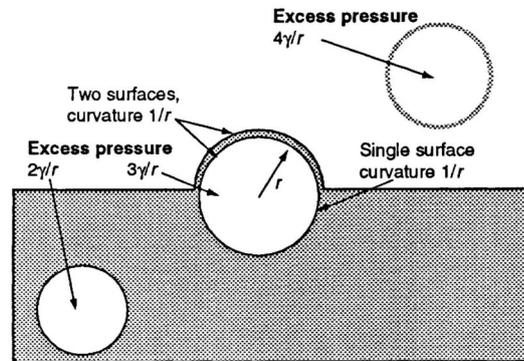


Figure 2.2: Bursting of a bubble and its excess pressure. S.D. Lubetkin, 1995 [8].

To have an entire overview, in an industrial electrolyzer,  $H_2$  and  $O_2$  are then captured in phase separators. In the optical electrolyzer experiment, however, the bursting bubbles release the respective gases into the nitrogen filled layer above the electrolyte surface. The gases will mix and then released through an exhaust pipe.

# 3 Electrolyzer

This section describes the high-pressure electrolyzer and which set up was used for the experiments. For this master thesis, the original equipment set up, as used previously [4], was modified in order to produce single bubbles and comply with the safety measurements. First, a brief explanation of the original configuration will be presented, followed by the description of the modifications.

## 3.1 Original configuration

The whole electrolyzer device is integrated by the optical electrolyzer, the KOH filling/draining circuit and the pressurizing gas feeding/exhaust circuit.

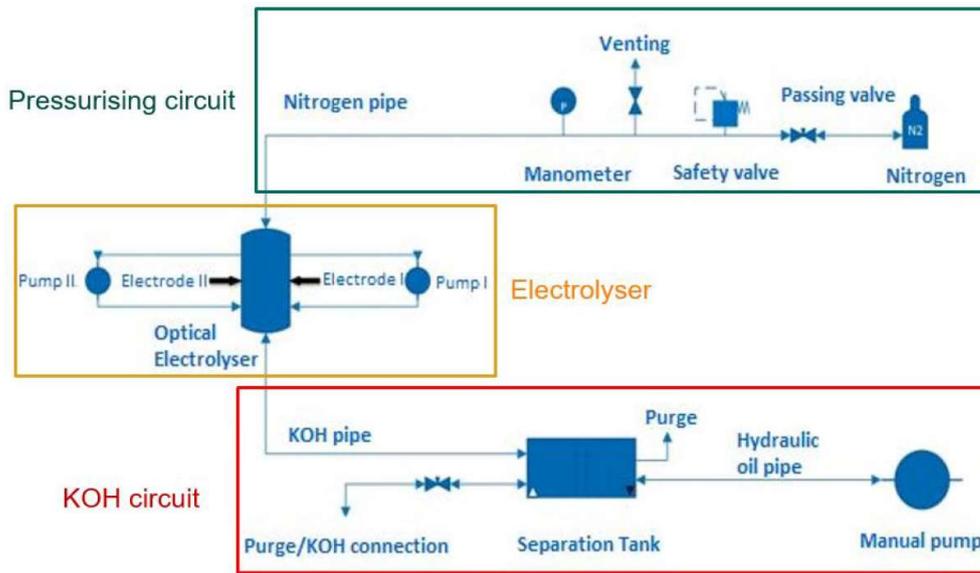


Figure 3.1: High-pressure electrolyzer scheme. Frey. [4]

The optical electrolyzer consists of a cylinder with two glass windows, which give the possibility to take optical measurements while the electrolysis process is ongoing.



Figure 3.2: Optical Chamber

The vessel provides eight access, which are used for different purposes:

- Two for placing the electrodes.
- One for filling/draining the chamber with the alkaline solution.
- One for feeding/exhausting the chamber with nitrogen/gases.
- Four are for the recirculation pumps.

The electrolyzer chamber is designed for working up to pressures of 450bar. The device has two configurations, with the first one, pressure can be increased up to 200bar, while the second configuration allows a maximum pressure of 450bar. For this series of experiments, only the first configuration is used. Despite the modifications, both configurations were maintained.

Electrodes are exchangeable in order to have different shapes and sizes. For this master thesis, new electrodes have been designed (see chapter 3.2.1).

Nitrogen is contained in a high-pressure bottle and fed in through the passing valve, which links the tube with the optical electrolyzer. A pressure gauge measures the total pressure of the system; also, a relief valve is installed, which actuates at the limit pressure of 210bar for configuration one and 500bar for configuration 2.

The hydraulic tank and the manual pump are used to increase the pressure above 200bar. The manual pump is connected to the hydraulic tank, which is connected to optical chamber. The tank has two separated circuits. The first one is filled with the electrolyte and connected to the electrolyzer chamber. The second circuit is filled with oil and connected to the manual pump. A piston inside this tank separates both liquids.

To go into more details about the electrolyzer construction and mechanical characteristics previous works are available, this topic is not presented here as is not the focus of this master thesis.

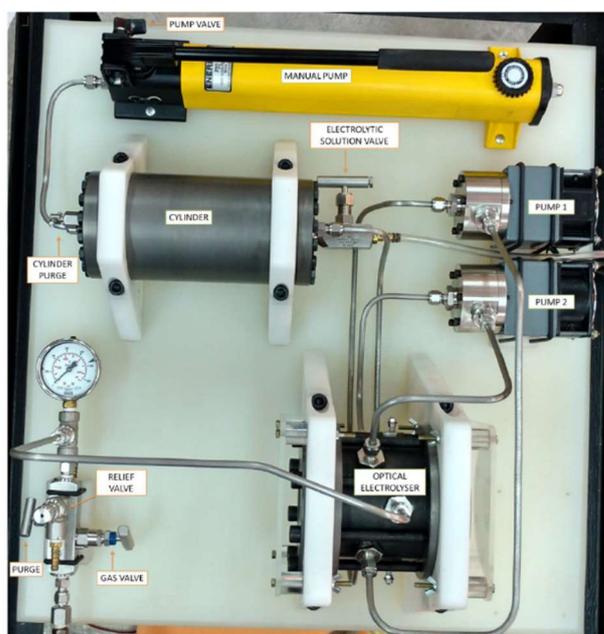


Figure 3.3: High-pressure electrolyzer – Original configuration.

## 3.2 New configuration and new electrodes

With the purpose of generating single bubbles and making possible a more accurate acquisition of the optical measurements, a modification of the electrolyzer and new electrodes have been developed and implemented in the frame of this master thesis. .

### 3.2.1 New Electrodes

As it was mentioned, the aim was to produce single bubbles; therefore, the design follows this objective. Moreover, the position where the new electrodes are inserted has been changed from the previous place in the original configuration. Now the electrodes are inserted from the bottom and not from the side position.

For the new electrodes, wires of 0.05mm were coated with glass and their tips were polished so to get a smooth surface. The polished surface makes possible to take an accurate measurement of the wire cross section area.

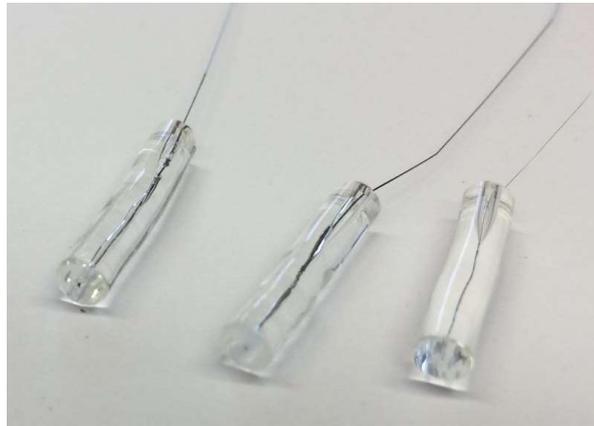


Figure 3.4: New glass coated wire electrodes.

To make possible the arrangement of the new electrode into the optical chamber, the glass coated wires were inserted into metal tubes, which are coupled to a connector. With this connector the electrode may be mounted at one of the access ports of the electrolyzer vessel. The wire passing along the metal tube is electrically insulated. The electrical connection to the power source is realized at the opposite end of the wire, which is outside the metal tube. Construction details are presented in Appendix B.

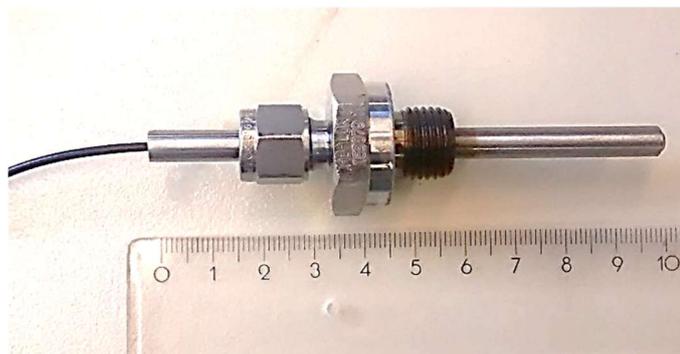


Figure 3.5: New electrode. Finished model.

### 3.2.2 New Electrolyzer set up

To make proper use of the new electrode design and optimize the single bubbles generation, a modification of the electrolyzer has been developed. Referring to the access points, labelled from 1 to 8, the original configuration is: 1 for the pressurizing gas feeding/exhaust; 2, 4, 6 and 8 for the recirculation pumps; 3 and 4 for the electrodes and 5 for the alkaline solution filling/draining.

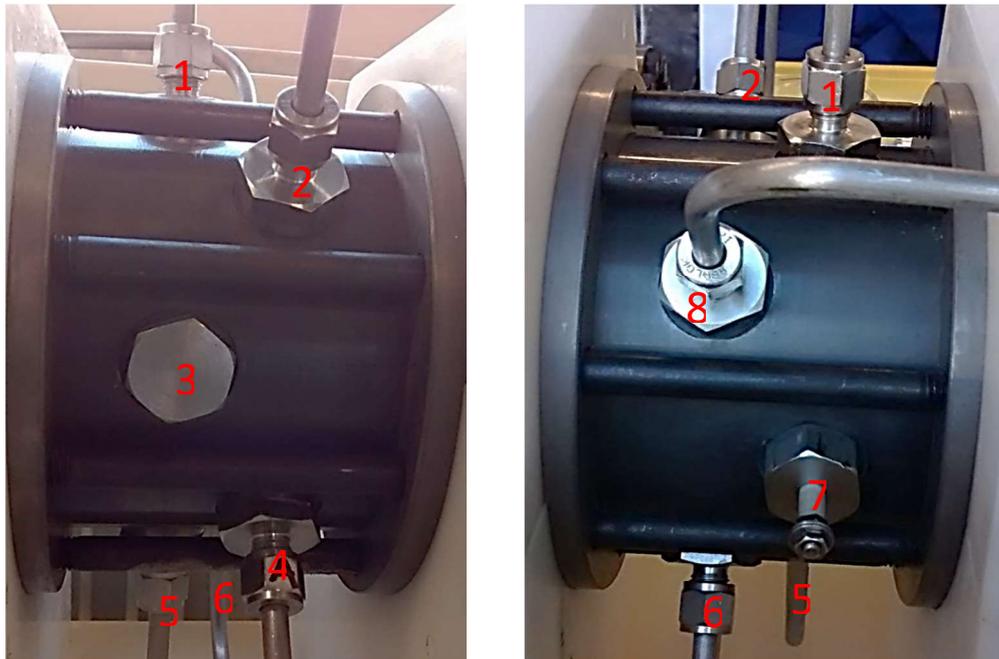


Figure 3.6: Optical chamber inputs, old configuration.

1: Gas feeding/exhaust - 2: Recirculation pump 1 outlet - 3: Electrode - 4: Recirculation pump 1 inlet  
5: Solution filling/draining - 6: Recirculation pump 2 inlet - 7: Electrode - 8: Recirculation pump 2 outlet

For the new configuration, the electrodes pair is composed of one new glass electrode and one electrode of the previous design [4]. The glass electrode is fixed from the bottom, at position 5, providing a horizontal position of the electrode surface. The electrode with previous design maintains its position, connection 7.

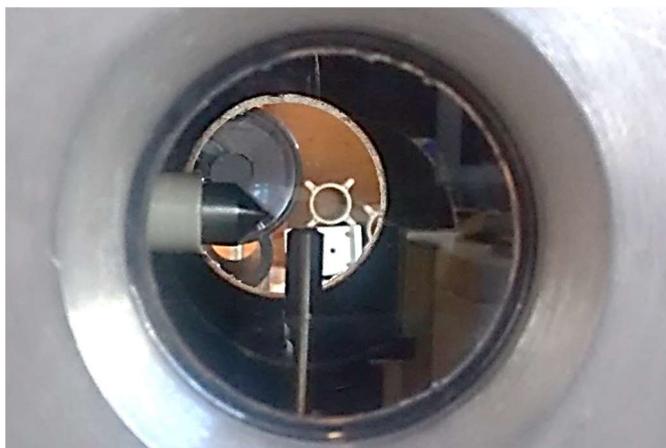


Figure 3.7: Optical chamber, electrodes new configuration.

As forced flow was not used, pumps are removed and so at position 2, 4, 6 and 8 plugs are connected. The solution is now filled through orifice at position 2. Position 1 remains the same with the purpose of feeding/exhausting the gas. The new configuration is shown in figures 4.7, 4.8 and 4.9.

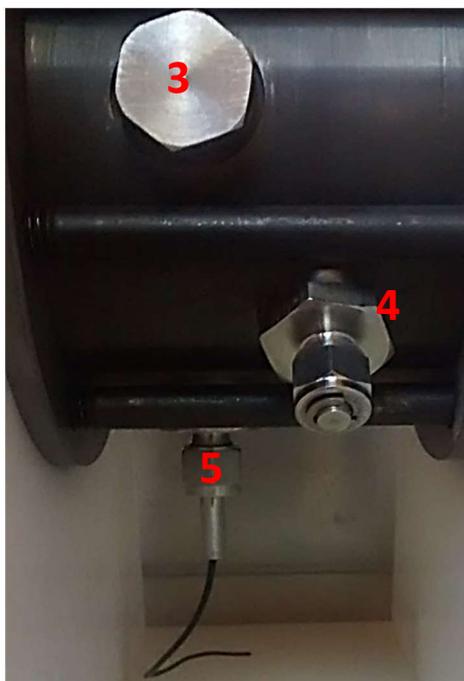


Figure 3.8: Optical chamber inputs, new configuration.

3: Plug - 4: draining - 5: Glassed electrode

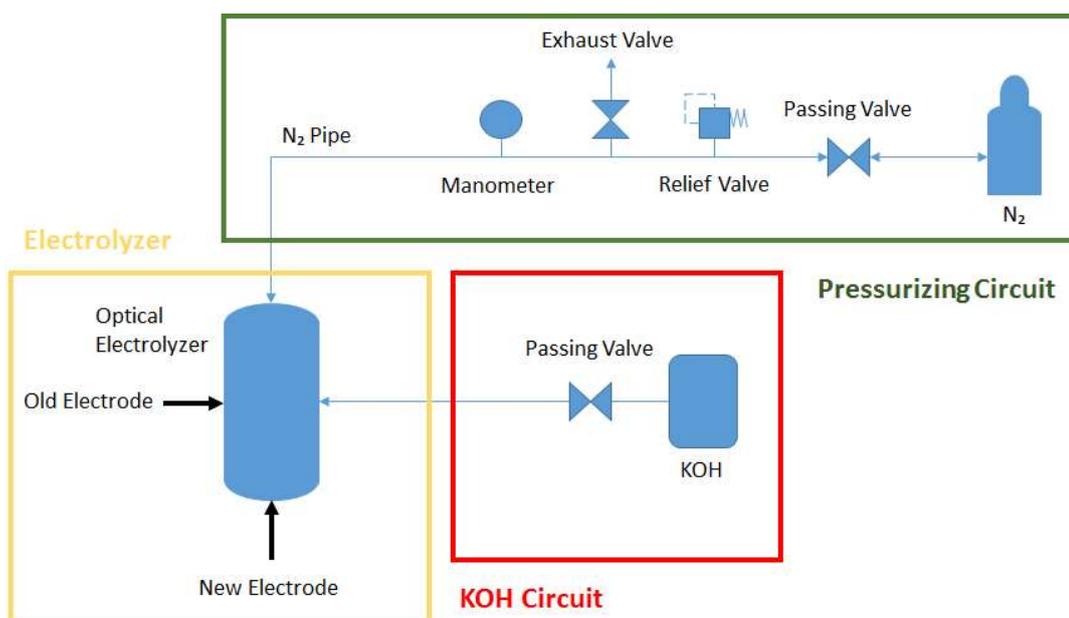


Figure 3.9: Electrolyzer Scheme, new configuration.

In order to test the new configuration and the new electrode at position 5, measurements were taken at atmospheric pressure.

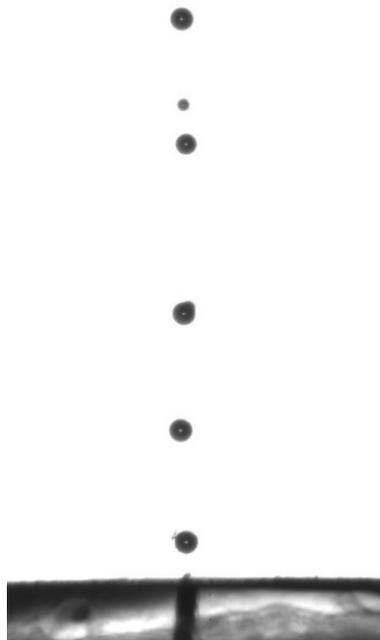


Figure 3.10: New electrode for single bubble generation with pulsed signal.

In Figure 4.10, bubbles production using the glass coated electrode at atmospheric pressure, with pulsed square signal of 1.8V amplitude, 10ms time pulse and 210ms period.

Qualitatively good results are achieved with this design. Single bubbles instead of bubble swarms may be investigated with the new set-up.

In the next section the auxiliary equipment and devices will be presented and described, and afterwards, in chapter 5 the safety analysis will be introduced.

## 4 Equipment

This section describes several auxiliary devices used for the operation of the experiments. Especially the optical electrolyzer, the power supply, optical measurements and data acquisition equipment were needed. For the current set-up, the following devices were used:

- High-pressure optical electrolyzer.
- Electrical source: Measurement Card - LabVIEW
- Double-pulsing-Nd:YAG Laser.
- CCD-Camera. Resolution of 1280 x 1024 Pixel.
- Computer: Coral II duo, 2Ghz, 3GB ROM.

### 4.1 Electrolyzer

Electrolysis is performed in the experimental optical high-pressure electrolyzer, which was developed at ITBA and set up at IKET. The electrolyzer was already tested and used in the previous work from Frey [4]. The device has been already described in section 3 as well as the modifications that were introduced during this master thesis. In appendix A, the electrolyzer manual.

### 4.2 Power Supply

A measurement card, which was controlled by LabVIEW Software, was used as electrical supply. The card can supply up to 10 Volts with different waveforms and it was use as well for taking voltage measurements. Introducing different voltages profiles had a strong positive influence on the single bubble formation.

The output square voltage signal and the measurements were controlled and display by LabVIEW. The current that circulates through the electrolyzer was calculated by measuring voltage on an intermediate resistance connected in between the source and the electrodes. With both values, voltage and resistance, current is calculated following equation (3.1), were  $I$  is the current,  $V_{res}$  is the voltage at the resistance and  $R$  the resistance value. In addition, voltage at the electrolyzer is calculated by taking a mesh over the circuit (3.2), for this case  $V_{el}$  is the voltage at the electrolyzer and  $V_{ps}$  is the voltage of the pulsed signal. Figure 3.1 shows the electrical circuit.

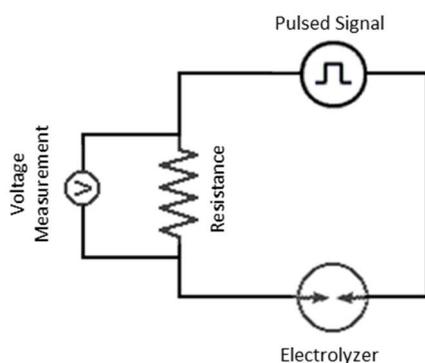


Figure 4.1: Electrical Circuit.

$$I = V_{res}/R \quad (3.1)$$

$$V_{el} = V_{ps} - V_{re} \quad (3.2)$$

Equations (3.1) and (3.2) are valid for direct current, what could not be applied in this case as the pulse is dependent on time, however, as the generation of hydrogen is instantaneous, it was supposed that D.C. is being applied when the pulse is active.

By knowing the current, generated amounts of hydrogen and oxygen per unit of time can be calculated, what is possible using equations (3.3) and (3.4) presented by Shen [17], where  $N$  is the moles per unit of time produced,  $i$  is the current density,  $A$  is the electrode surface, and  $F$  the Faraday's constant.

$$N_{O_2} = \frac{i A}{4 F} \quad (3.3)$$

$$N_{H_2} = \frac{i A}{2 F} \quad (3.4)$$

For the risk assessment it is important know how much hydrogen and oxygen is produced in order to avoid combustion or even detonation in the electrolysis cell. This issue will be treated in the safety related section.

### 4.3 Optical equipment

In order to take optical measurements, the laser Double-pulsing-Nd:YAG and the CCD-Camera, coupled with a microscope, were used. Both devises are connected to the lab computer and controlled with DAVIS 7.2 software, which manage the triggering of the laser, the acquisition of the images by the camera and the storage of the data.

#### 4.3.1 Laser

For illuminating the bubbles, a double-pulsing-Nd:YAG laser, with wavelength of  $532nm$ , is combined with a diffuser. The double pulsating function of the laser gives the possibility of taking two consecutive pictures with minimum time delay. This function is used to calculate velocities of the particles. The diffuser ensures a homogeneous illumination inside the vessel, then, bubbles in the observation range are all equally illuminated. In this case the high efficiency diffuser is used, which has a dye plate. The diffuser diameter can be adjusted, corresponding to an illumination area, following equation (3.5), given in the user manual [18], the diameter of this area is calculated.

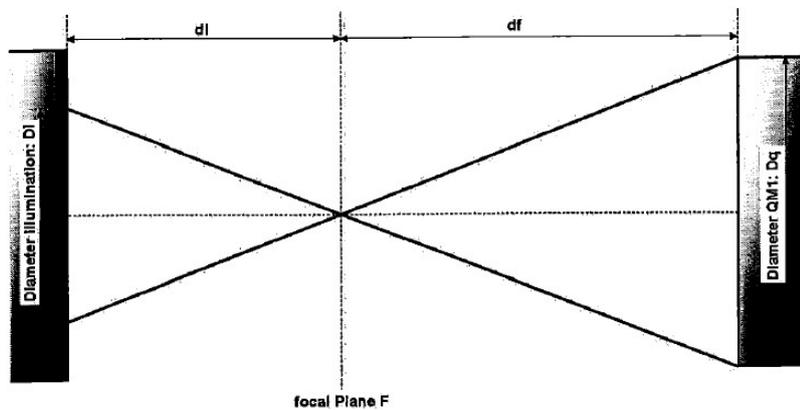


Figure 4.2: Optical beam path scheme. LaVision, 2016 [18].

$$D_i = \frac{D_q d_i}{df} \quad (3.5)$$

Where  $D_i$  is the diameter of the illumination area (diffuser plate),  $d_i$  is the distance from the diffuser to the focus,  $D_q$  is the microscope's diameter and  $d_q$  the distance between the microscope and the focus. In this case,  $D_i$  has a value of approx. 19.5mm.

### 4.3.2 Camera

The applied CCD-Camera (Charge Coupled Device) has resolution of 1280 x 1024 *Pixel* (FlowMaster 3S, LaVision). The resolution of the camera is of  $2.5\mu\text{m}/\text{pixel}$ , and its observation window is  $3.17\text{mm}$  per  $2.52\text{mm}$ , wide and high correspondingly. Images captured by the camera can be instantaneously displayed at the computers monitor.

### 4.3.3 Microscope

The Questar QM1 long distance microscope is coupled to the camera. As is it mentioned in the product manual, the microscope is recommended for detecting particles in the range of  $5\mu\text{m}$  to  $500\mu\text{m}$ , and has working distances in between 560mm and 1520mm [18].

### 4.3.4 Calibration

Before taking any measurement, devises were calibrated. The focus of the microscope was set at a distance of 575mm, where the tip of the electrode was reached. The laser was placed 100mm from the focus. Following the instructions of the user manual, the pictures size was calibrate. A scaling plate was used, an image of it was taken, and then displayed at the software interface. Calibration was done using this images and the specific software tool. Finally, the scale is set, and the following taken images maintain this configuration.



Figure 4.3: Taken Image of the scaling plate.

### 4.3.5 Taking Images

Images of the bubbles can be taken since the electrolyzer has two glassed windows, making it possible to look at the inside. Electrolyzer, laser and camera are arranged in the same horizontal axis, the laser is placed directly pointing to one of the glassed windows, and then the camera captures the pictures through the opposite one. Position of the laser and camera can be adjusted in both horizontal and vertical position, giving the possibility of a better resolution.

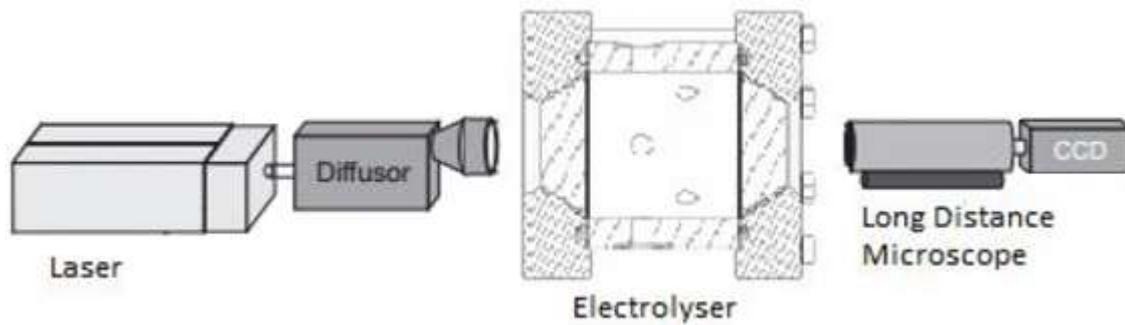


Figure 4.4: Electrolyzer, laser and camera scheme. F. Frey, 2016 [4].

The software controls and triggers the laser and the camera. Images are stored also by the software, then they are extracted and analyzed. Images are taken with a frequency of 2Hz, the laser has two cameras, what making possible to take two consecutive images with a time delay of 11000 $\mu$ s. Therefore, for 200 camera shots, 400 images will be acquired, 100 seconds are needed per sample. Figure 3.5 shows both consecutive pictures.

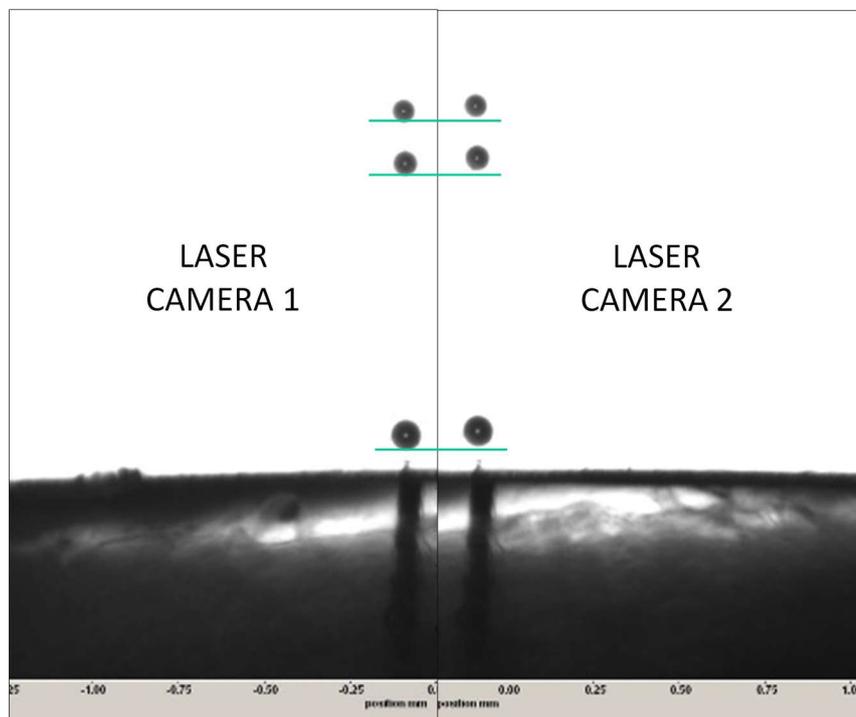


Figure 4.5: Consecutive images taken by laser cameras 1 and 2 with a time delay of 11000 $\mu$ s.

# 5 Safety Analysis

In order to provide a safe working environment with the electrolyzer experiments, a safety analysis has been performed at the beginning of the master thesis. The main objective was to generate a hazard assessment. And intrinsically safe operational instructions for the experiments. IKET personnel provided the template for the risk assessment, which is found in Appendix C. All the hazards were listed taken into account personnel and equipment safety. The main detected hazards were:

- KOH solution handling
- High working pressures
- Hydrogen and oxygen generation in closed vessel.

Consequences which came out from the safety analysis, affected cleaning and maintenance, modification of the equipment, physical protection measurements and analysis of the hydrogen production.

## 5.1 Potassium Hydroxide Solution

Potassium hydroxide solution is known as a strong base. All the safety measurements related to its handling are given in the corresponded data sheets, which can be found in Appendix D. The final deposition of the solution follows the “General safety regulations - KIT Campus North” [19].

## 5.2 Cleaning and Maintenance

It has been noticed that remains of electrolyte reacted with the electrolyzer surface. White powder was found over exterior surface, mainly in one of the electrodes orifice, on the solution valve and inside the optical chamber.

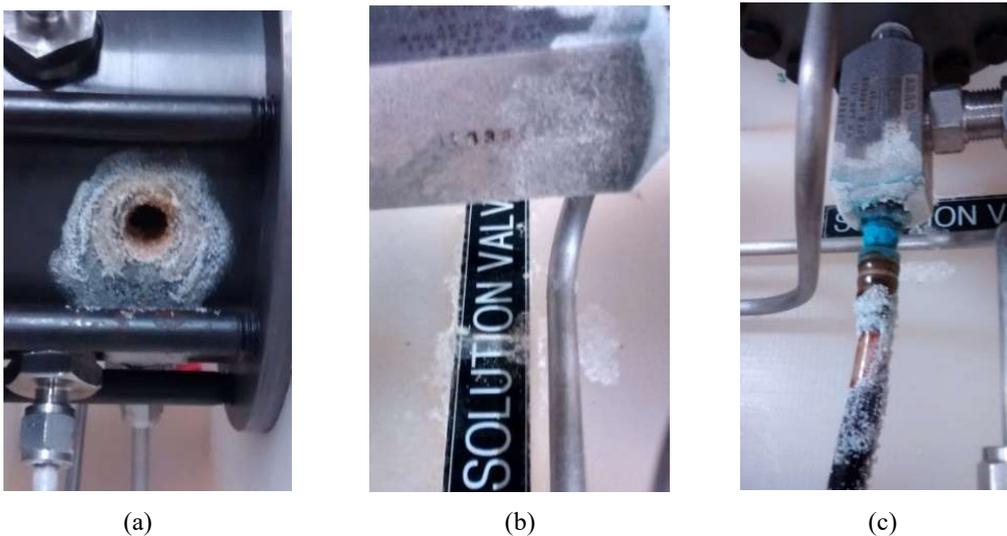


Figure 5.1: Electrolyzer surface - (a) Hole for electrode. (b), (c) Solution Valve.

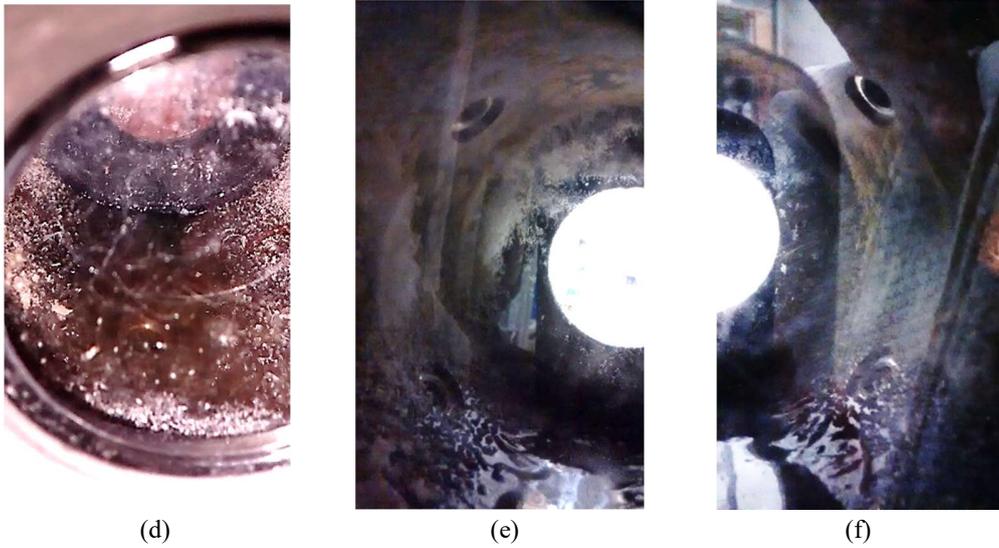


Figure 5.2: Optical chamber – (d) Lens. (e), (f) Vessel interior.

For the electrolyzer cleaning, a series of instructions was suggested by ITBA in order to clean appropriately the exterior and interior of the equipment. It is important to clean the equipment, also tubes, plugs and electrodes after performing the experiments to avoid the incrustation formation. In Appendix E can be found more detailed information about the cleaning procedure. Figure 5.3 shows the electrolyzer after the cleaning.

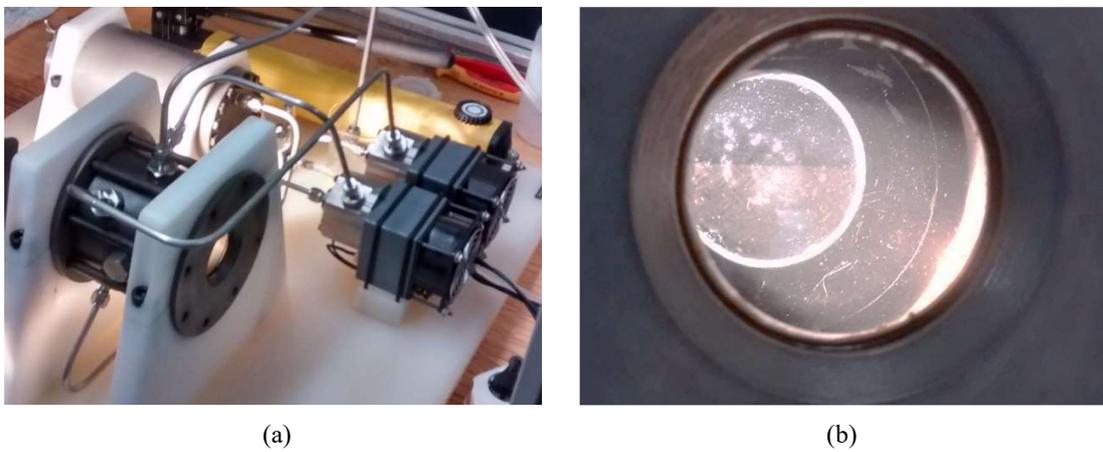


Figure 5.3: Electrolyzer after being cleaned – (a) Device. (b) Optical chamber

## 5.3 Modifications

In order to increase the safety of the equipment operations, some modification were proposed and implemented (see Appendix E).

### 5.3.1 Container

A container was designed in order to give mechanical protection while working with high pressures and contain any KOH solution leakage. The drawing of the container is found in Appendix B.



Figure 5.4: Metal sheet container.

### 5.3.2 Gas Valve

As shown Figure 5.5 the pressure gauge and valves are now outside the electrolyzer panel, this modification was introduced due to the safety analysis. The main idea is to have a separation wall between the optical chamber, which is pressurized, and the manual valve.

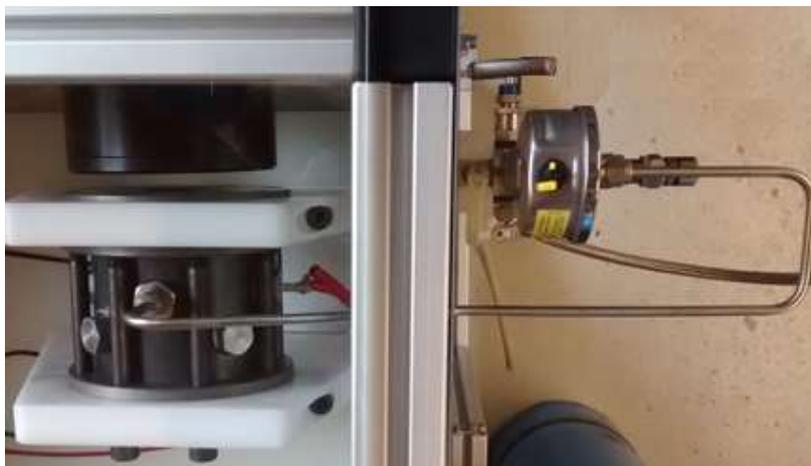


Figure 5.5: Optical chamber, pressure valves and gauge – New connection.

### 5.3.3 Exhaust Valve

The exhaust valve has a plastic tube, as KOH solution can be contained in the exhaust gases, it is proposed to use a canister where the solution droplets can be deposited in case some of them came out with the gases.

## 5.4 Hydrogen Production

An important issue for the safety analysis was the hydrogen and oxygen production and the possibility of their reaction, since the gases are being produced at the same time, at stoichiometric concentrations, mixed into the nitrogen phase at high pressure and inside the closed vessel. Therefore, the inventory has to be controlled.

The aim is to know how much time the electrolysis can be run before hydrogen concentrations reach the lower flammability limit. From [Kumar 1985] it can be shown that in nitrogen diluted  $H_2 - O_2$  mixtures the flammability limit is reached with 4% of  $H_2$ .

In order to obtain the operation time, two different simulations were done, which are presented in appendix F. Here, a brief calculation is presented in order to show that the operational time was long enough to take a round of measurements. These are the parameters and assumptions that were taken into account:

- Atmospheric pressure
- $H_2$  Lower Flammability limit: 4% nitrogen, accompanied with 2%  $O_2$
- 0.2 Liters of  $N_2$  volume inside the vessel.
- 4 – 4.5 kWh/Nm<sup>3</sup> $H_2$  efficiency of the electrolysis.
- Power calculation:  $P = VI$
- Maximum power input:  $3.8mW = 1.9V * 2mA$

The production of hydrogen is calculated taking into account the power input and the energy consumption, then the time is estimated by knowing until which point the hydrogen production reaches the 4% of volume in the 0.2 liters. As a result, the maximum operational time for the electrolysis cell without purging is approximately 9 hours.

# 6 Experimental Measurements and Parameters

In this section, the actual measurements are presented. Also the parameters that defined the conditions under which the optical measurements were taken.

## 6.1 Experimental Set-Up

Before starting the experiments, preparation of the device and safety measurement were observed. A checklist is provided in order complete the procedure correctly. The checklist can be found in the safety analysis, which is attached in Appendix C, also the manuals are found in. The procedure follows the following steps:

- Electrolyzer power supply, optical equipment and computer are checked, turned on respectively.
- Data acquisition is tested.
- Electrolyzer filled with KOH solution and pressurized with nitrogen.
- Power supply is turned on.
- Measurements are taken and saved in the computer.
- Electrical source and optical equipment are turned off.



Figure 6.1: Experimental Set up.

## 6.2 Parameters

Power supply and pressure were the main input parameters that, in the present experiments, determination the bubble formation. In Appendix G, a table can be found with the different measurement that were performed. The potassium hydroxide solution concentration is also a variable to take into account, however, for this round of experiments the concentration was maintained constant (see below).

### 6.2.1 Power Supply

The use of square signal gave the possibility of characterizing the power input signal with more detail. Voltage amplitude, time of the pulse and period are the main characteristics. For the same working pressures, different power input was used by varying the mentioned parameters. A relationship between the bubble size and power input could be observed.

### 6.2.2 Working Pressures

In the experiments the applied working pressures has been varied between 1bar and 180bar. The actual pressure level at which the measurements were taken were: 1bar, 20 bar, 40bar, 60bar, 80bar, 140bar, 180bar.

### 6.2.3 Potassium Hydroxide Solution

For all the performed experiments, potassium hydroxide was used as electrolyte. Its concentration was always maintained at 23.5%*vol*.

## 6.3 Optical measurements

Moreover, optical measurements were taken, the resulting images were then processed with an image software analyzer. From the analysis of the images, bubble size, rising velocity and time life of the bubbles at the free surface are obtained, and as the working pressure and power input are known, all this variables can be related.

### 6.3.1 Images

Images are acquired and saved, then processed and analyzed. The pictures are saved with JPG extension and have 1360 x 1070 pixels, at the frame of the image the scale in millimeter is shown, giving the possibility of calibrating the image with the software analyzer IMAGE J.

### 6.3.2 Processing the images

The first step to process the images was to set and scale. A linear object, set by IMGAE J, is defined and measured on the image scale bar, giving as result the relation of pixels per millimeters, which result in 392 pixels/mm, therefore, the real recorded size was 3.47 x 2.73 mm corresponding to 1360 x 1070 pixels.

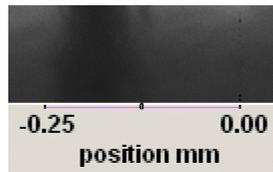


Figure 6.2: Liner object at image scale bar.

Secondly, the black/white threshold has to be applied. IMAGE J gives the possibility of, manually or automatically, adjust the image threshold in order to detect the bubbles and analyze them. The threshold defines a range, in between 0 (black) and 255 (white), in order to separate the objects of interest from the background. Pixels with values under the threshold are converted to black and, on the other way around, pixels with values above the threshold are converted to white. With this function, bubbles could be clearly separated and easily identified in the particle analysis tool [22].

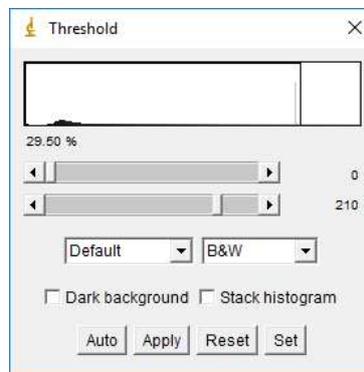


Figure 6.3: IMAGE J threshold interface.

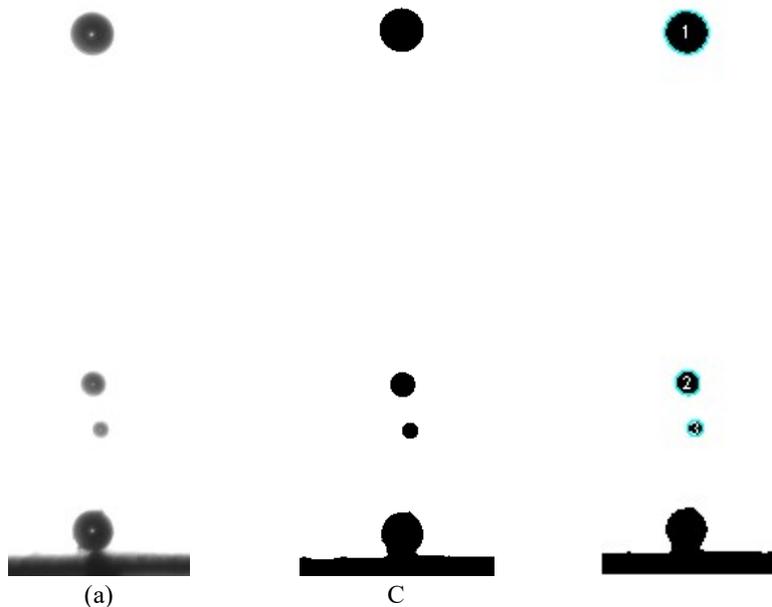
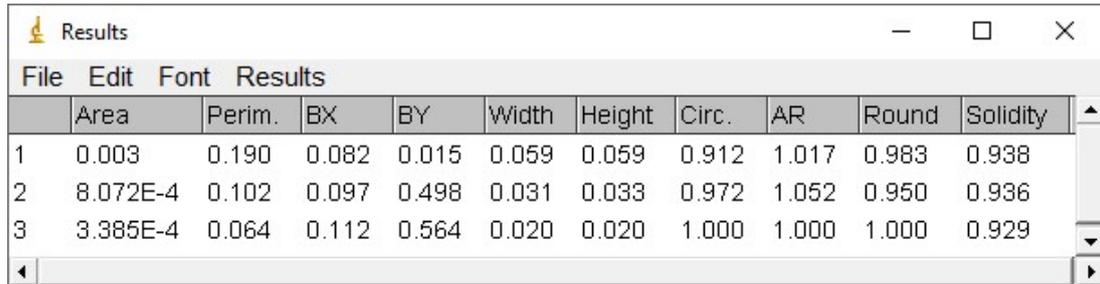


Figure 6.4: Image processing - (a) Image taken by the camera, (b) image after applying the threshold; (c) Detected bubbles after using the particle analyzer tool.

### 6.3.3 Analyzing the images

Bubbles were analyzed with the analyze particle tool, which detects the particles previously defined by the threshold. Bubbles are detected and measured automatically. Finally, a table displays different variables characterizing the bubbles. The displayed variables can be defined by the user according to what is needed to be analyzed, in this case, position in x- and y-axis, their area, perimeter, wide, high and shape characteristics of each bubble was obtained.



The screenshot shows a window titled 'Results' with a menu bar containing 'File', 'Edit', 'Font', and 'Results'. Below the menu bar is a table with 11 columns: 'Area', 'Perim.', 'BX', 'BY', 'Width', 'Height', 'Circ.', 'AR', 'Round', and 'Solidity'. The table contains three rows of data for particles 1, 2, and 3.

	Area	Perim.	BX	BY	Width	Height	Circ.	AR	Round	Solidity
1	0.003	0.190	0.082	0.015	0.059	0.059	0.912	1.017	0.983	0.938
2	8.072E-4	0.102	0.097	0.498	0.031	0.033	0.972	1.052	0.950	0.936
3	3.385E-4	0.064	0.112	0.564	0.020	0.020	1.000	1.000	1.000	0.929

Figure 6.5: Results of analyzed particles by IMAGE J.

IMAGE J has the option of programming routines with MACROS, automating the application of the threshold and the analysis of the particles for each image. To define the correct threshold, bubbles diameters were first manually measured with other function provided by IMAGE J, then the range of the threshold was defined in order to obtain the same results as with the manual analysis. Ranges from 0 to 195 and 45 to 245 were applied.

Finally, after the particle analysis, the MACROS routine saves the measurements as an Excel file.

In order to process the information and automatized the measurement of the bubble diameter and the calculation of their rising velocities, an Excel MACRO was programmed. In the case of the residence time at the free surface, no automatized routines could be applied.

Basically the Excel MACROS collects into one Excel Sheet all the information that was obtained from the IMAGE J's MACROS. Then, the information is processed in order to obtain results. Different filters and routines were applied.

Finally, the Excel sheet displays different graphs and statistical values referring to the actual case. The results will be presented in the following section.

#### 6.3.3.1 Bubble size

Bubble size was determined by analyzing the information obtained from the image software analyzer. In this case only the output data from camera 1 was processed, as the corresponded photo from the second camera is not adding any new information to the analysis.

In order to obtain the bubble size distribution, the Excel sheet applies first four filters with the objective of detecting if the information that is being analyzed belongs to a bubble or some other particle, like dirt. Regarding the output variables from IMAGE J, the filters use the area, perimeter, wide, height and shape characteristics.

Finally, statistical functions are applied to previously filtered information, graphs and statistics variables, are presented as results.

The bubble size distribution was obtained for different working pressures and different electrical input signals. Thus it, was possible to characterize the bubbles size in relation with both mentioned variables.

### 6.3.3.2 Rising velocity

For calculating the rising velocity the corresponding pair of images from camera one and two were processed. After processing the images, the difference in the vertical position of each bubble was obtained. As the time laps between the displacements is known to be  $11000 \mu s$ , the velocity is easily calculated via.

$$C_y = \frac{y1 - y2}{11000 \mu s} \quad (6.1)$$

As in the case of the bubbles size, same filters are applied for detecting the bubbles information. The difficulty here is to make sure that the information from the different cameras correspond to the same bubble. In order to make this possible, the program has a second stage where the information from both cameras is compared. After the information is checked, mainly by comparing bubbles wide, height and x-axis position, equation (6.1) is applied.

Finally a distribution of the rising velocity is obtained. The single bubble generation made easier to perform the velocity analysis. Statistics are also performed, graphs and variables are generated within the Excel sheet.

### 6.3.3.3 Life time at free surface

In this case, only observation were done in order to characterize the relationship between the bubble diameter and how much time the bubble stays at the free surface. For this purpose, a vertical configuration of the electrolyzer vessel was used. Images from the plain view of the free surface were taken and further analyzed.



Figure 6.6: Vertical configuration

## 6.4 Error

The image software analyzer introduces some error, although the applied threshold was tested in order to obtain the same bubble diameters as other method also provided by IMAGE J. All these are functions of IMAGE J, and there is no comparison with other software. A consequence of the applied threshold, the bubble might be not well represented, giving as a result different values of diameters for the same bubble. This error was estimated to be  $\pm 3\mu m$ . This error was introduced in the calculation of the rising velocity, which resulted in an estimation of about  $\pm 0.27 mm/s$ .

Moreover, the position of camera 1 and camera 2 can introduce some error. They present a slight displacement, this means that the electrode surface is not always at the same point of the vertical scale. However, this correction was done.

Finally, in the case of pressure, the pressure gauge and depressurization can influence the measurements. A stochastic error of 5% was assumed for the pressure measurements. This value was taken from the sensor specification.

# 7 Results

In this section, the results are presented, graphs and tables are shown as summaries. The results are organized in different sections highlighting the bubbles size, rising velocity and lifetime at free surface. In each of these sections, differentiation between atmospheric and high pressure is done.

## 7.1 Bubbles size

The bubble diameter was characterize by the arithmetic mean, mode (an interesting point was to see which was the most repeated diameter value) and standard deviation, for each case, a histogram is presented. The histogram shows frequency of distribution at a constant pressure and power supply signal.

With respect to Figures (7.1), showed above, and all the following histograms, the blue columns represent the how many bubbles are included in a certain diameter range of diameter. The orange line accumulates number of detected bubbles.

### 7.1.1 Atmospheric pressure

For this case most measurements were taken as bubbles were clearly detected. The voltage range was from 1,5V to 1,9V in steps of 0,1V. The pulse time and period vary for the different amplitudes. In Appendix G, the measurement plan and signal characterization is presented.

#### 7.1.1.1 Hydrogen

First, the correspondent histograms from 1,5V to 1,9V are shown. Statistical values are presented at the end in a summary table.

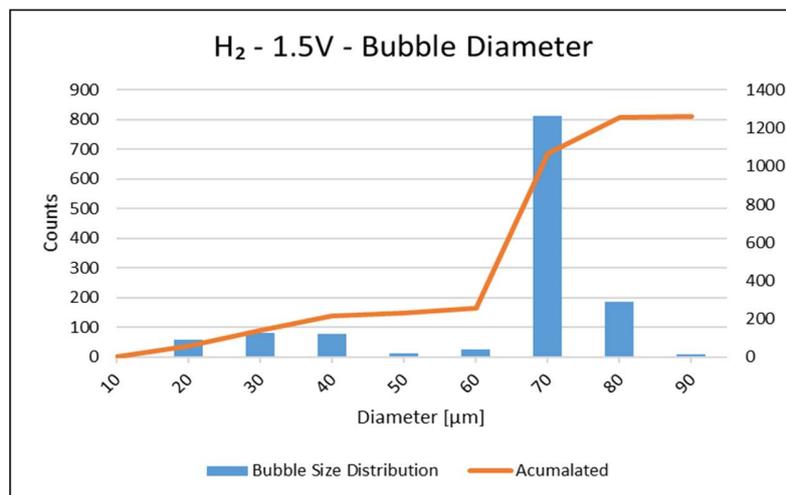


Figure 7.1: H<sub>2</sub> diameter distribution – 1.5 Volts, Period 450ms, Pulse time 50ms – 1 bar

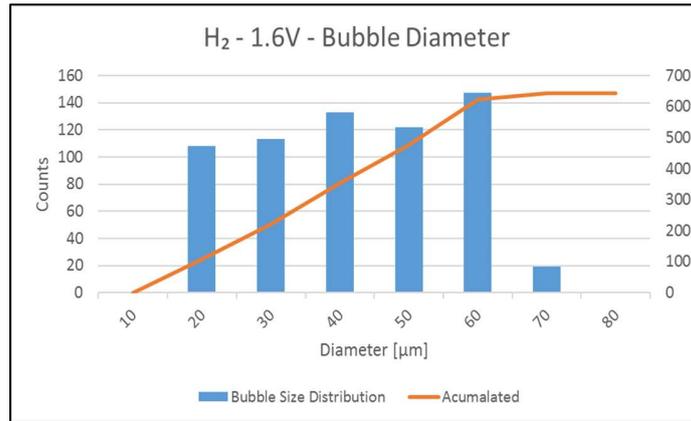


Figure 7.2: H<sub>2</sub> diameter distribution – 1.6 Volts, Period 510ms, Pulse time 10ms – 1 bar

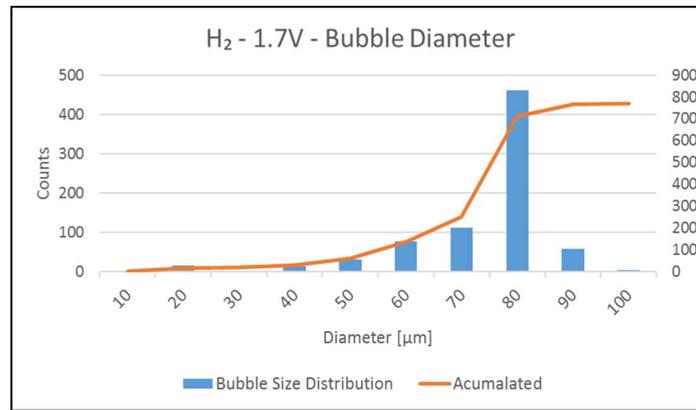


Figure 7.3: H<sub>2</sub> diameter distribution – 1.7 Volts, Period 210ms, Pulse time 10ms – 1 bar

For 1,7V the pulse period was shorter in order to approximate to a bubble swarm behavior. The corresponding results have shown differences in comparison with the other applied voltages at atmospheric pressure. The results are presented in the following paragraphs.

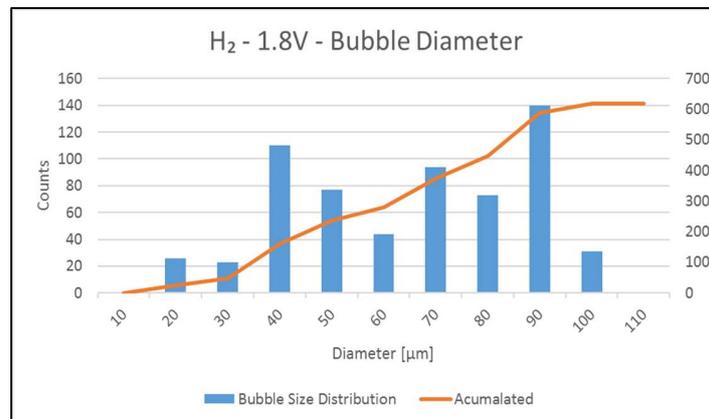


Figure 7.4: H<sub>2</sub> diameter distribution – 1.8 Volts, Period 510ms, Pulse time 10ms – 1 bar

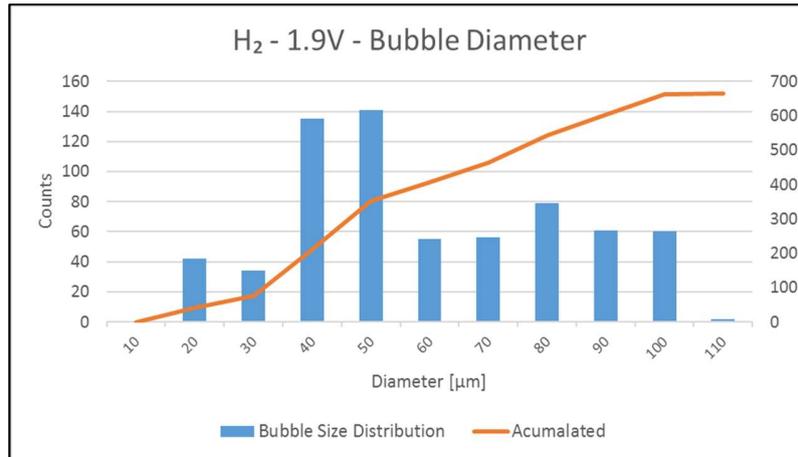


Figure 7.5: H<sub>2</sub> diameter distribution – 1.9 Volts, Period 710ms, Pulse time 10ms – 1 bar

In table 7.1 a summary of the results is presented, where the signal parameters, diameter’s mean and mode and STD are indicated.

Table 7.1: Summary of the hydrogen bubbles diameter results at 1bar.

Hydrogen - 1 bar					
Volt. [V]	Pulse t [ms]	T [ms]	Mean [μm]	Mode [μm]	STD
1.5	50	450	59.7	64	13.87
1.6	10	510	37.52	56	14.74
1.7	10	210	68.69	74	12.92
1.8	10	510	60.11	37	22.05
1.9	10	710	54.5	36	22.88

By giving a first look at the results in table 7.1, simple conclusions do not seem to be straightforward. In the case of 1,5V, the mean and mode are near to each other, also in the case of 1,7V, what shows that the bubbles diameters are mostly around the mean and mode values, and few amount of bubble are outside this range.

However, for 1,6V, and especially for 1,8V and 1,9V, the differences seem quite important. This can be seen with the standard deviation value, which values are higher. To have a better understanding of what is happening, images were analyzed with more detail. Until now, there was no hypothesis relating the current pulse and the bubble formation. The first hypothesis could be that one pulse produces exactly one detached bubble. Alternatively one can assume that one pulse produces multiple detached bubbles. Finally, it may have happened that more than one pulse is needed to generate one detached bubble. Knowing the period of the pulsed signal and that the laser frequency is 2Hz, was possible to detect how many pulses between photos were supplied to the electrode.

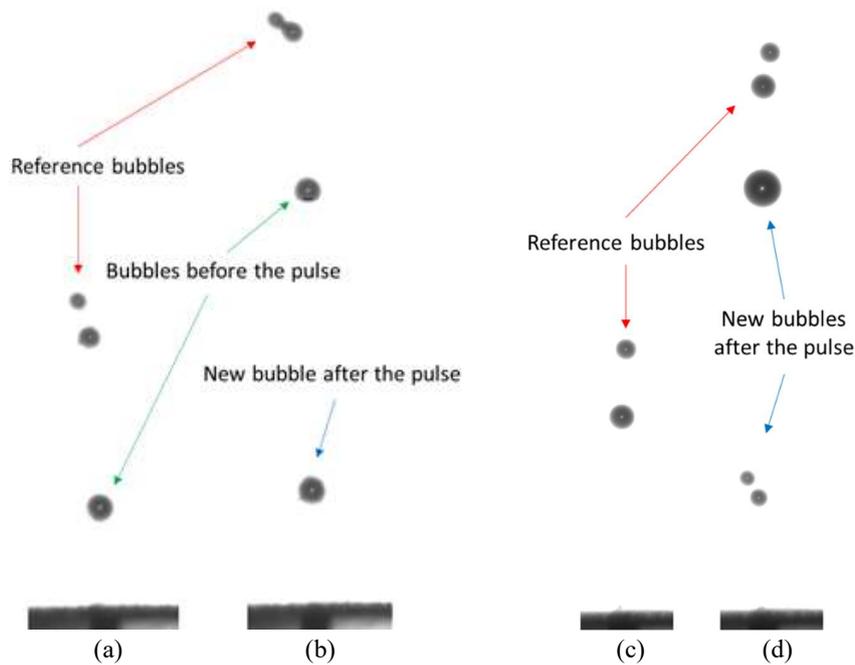


Figure 7.6: Analysis of the images, reference and new bubbles in consecutive pictures - (a) and (b) for 1,5V; (c) and (d) for 1,8V.

Figure 7.6 shows cases for 1,5V and 1,8V as an example of analysis. Then, for each case one hypothesis was generalize. In the case of 1,5V and 1,7V, one pulse generates one bubble, for 1,6V, 1,8V and 1,9V one pulse generates more than one bubble. For the last cases, the volumes of the bubbles generated by one pulse was measured from the images and summed up, with the total volume the ideal diameter,  $D_i$ , was calculated. This variable represents the diameter that would have one single bubble produces by one pulse. In table 7.2 results are shown.

Table 7.2: Single bubble production per pulse.

Hydrogen - 1bar					
V [V]	I [mA]	P [mW]	$D_i$ [ $\mu\text{m}$ ]	Vol [ $\text{m}^3$ ]	n [mol]
1.5	0.020	0.03	61	1.19E-13	5.30E-12
1.6	0.123	0.20	64	1.43E-13	6.36E-12
1.70	0.183	0.31	75	2.1E-13	9.46E-12
1.80	0.331	0.59	91	3.84E-13	1.71E-11
1.9	0.416	0.79	98	4.84E-13	2.16E-11

Table 7.2 shows the applied voltage, current, power, ideal diameter, the volume and the generated hydrogen moles. As the volume is known, even when more multiple bubble were measured, as well as the ambient conditions, the number of produced moles was calculated. Then, using equation (3.3), the current could be obtain, and assuming that in the short period of the pulse equation (7.1) can be used, the power was calculated. Thus, was possible to characterize the ideal diameter as function of the voltage, what is shown in figure 7.6.

$$P = VI \tag{7.1}$$

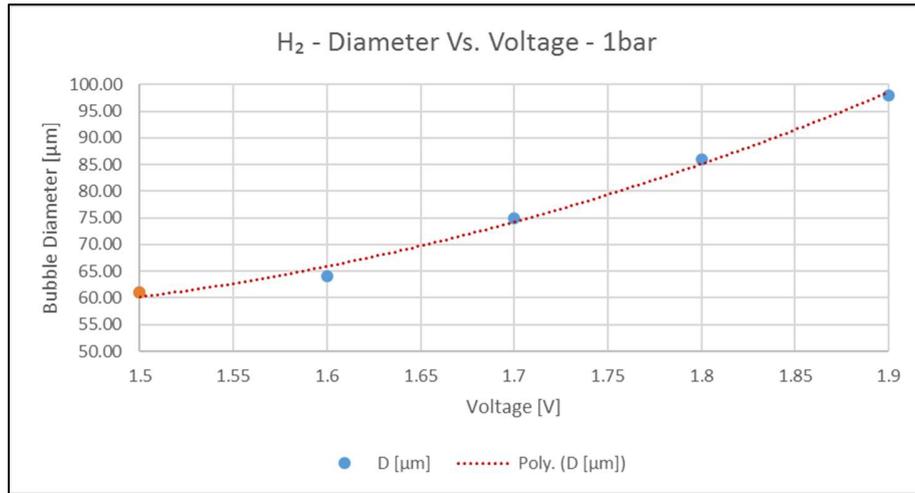


Figure 7.7: Single hydrogen bubble diameter per pulse vs. applied voltage

To sum up, it was observed that the input signal influences the bubble size. For the same pressure, different diameters were obtained for different voltages. As a second conclusion, for lower voltages, one pulse produce one bubble. More than one bubble of different sizes are generated at higher voltages giving a wider distribution of diameters values. The ideal diameters value is included in the distribution as the upper limit.

Moreover, 1,5V is applied during relatively long 50ms, what may have an influence on the ideal diameter. If this voltage would be only maintained for 10ms, less hydrogen will be produced and so the diameter would be smaller. Making a linear projection taking into account values from 1,6V to 1,9V, equation (7.1) for the ideal diameter may be obtained.

$$D_i = \frac{110}{V/mm} V - 111.5mm \quad (7.1)$$

Following the projection, the ideal diameter for 1,5V during 10ms is 53.5µm.

### 7.1.1.2 Oxygen

The same analysis is done for oxygen bubbles.

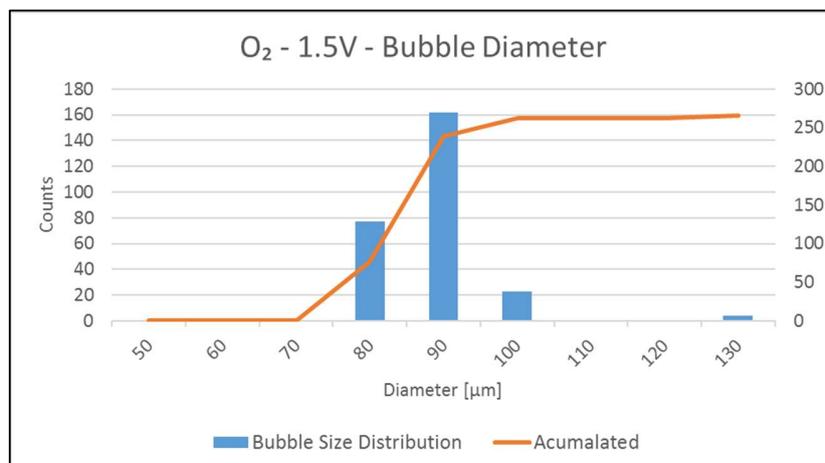


Figure 7.8: O<sub>2</sub> diameter distribution – 1.5 Volts, Period 450ms, Pulse time 50ms – 1 bar

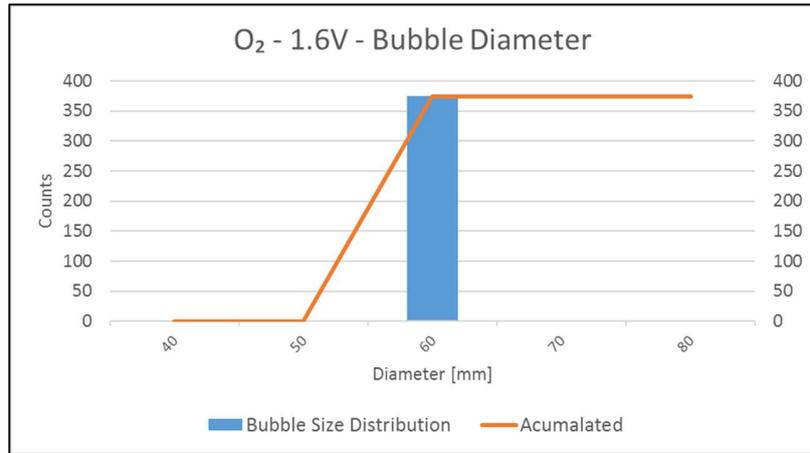


Figure 7.9: O<sub>2</sub> diameter distribution – 1.6 Volts, Period 510ms, Pulse time 10ms – 1 bar.

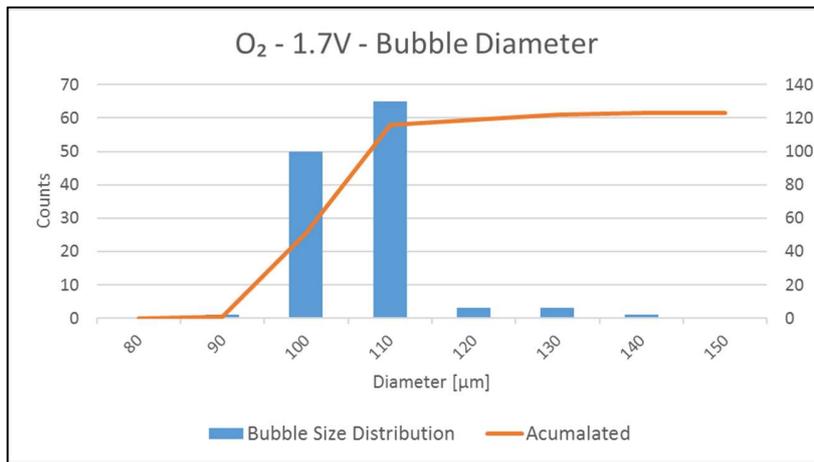


Figure 7.10: O<sub>2</sub> diameter distribution – 1.7 Volts, Period 210ms, Pulse time 10ms – 1 bar.

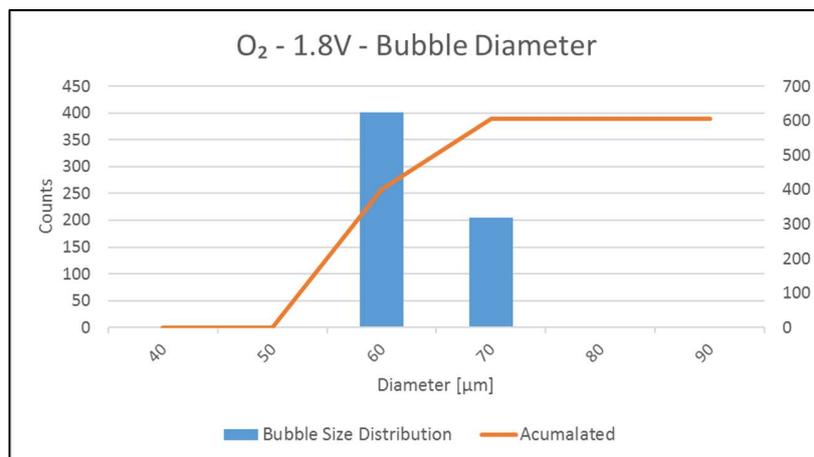


Figure 7.11: O<sub>2</sub> diameter distribution – 1.8 Volts, Period 510ms, Pulse time 10ms – 1 bar.

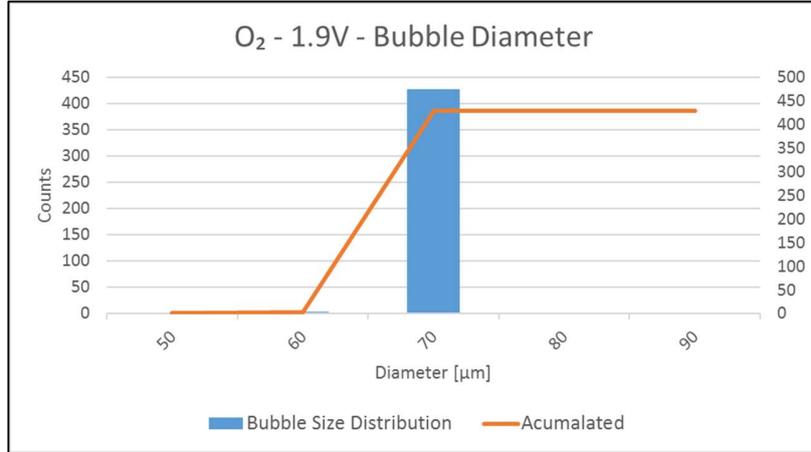


Figure 7.12: O<sub>2</sub> diameter distribution – 1.9 Volts, Period 710ms, Pulse time 10ms – 1 bar.

As in the case of hydrogen bubbles, the same analysis was made for oxygen, table 7.3 shows the summary of the results.

Table 7.3: Summary of the oxygen bubbles diameter results at 1bar.

Oxygen - 1bar					
Volt. [V]	Pulse t [ms]	T [ms]	Mean [μm]	Mode [μm]	STD
1.5	50	450	83.9	79	8.14
1.6	10	510	54.3	54	1.37
1.7	10	210	100.87	102	7.44
1.8	10	510	59.02	59	1.78
1.9	10	710	63.1	61	1.85

Table 7.3 shows that the sizes of the oxygen bubbles present a narrowed distribution; this can also be seen in the histograms. Furthermore, the images were also analyzed in order to understand the relationship between the current pulses and the bubble formation.

For the oxygen case, pulses of 1,5V, 1,6V, 1,8V and 1,9V generate one single bubbles. Only the 1,7V signal generated bubbles that required more than one pulse. From the photos analysis it came out that approximately seven pulses were needed before the bubble detaches. As in the case of hydrogen, the ideal diameter, which is showed in table 7.4, was calculated.

Table 7.4: Single bubble production per pulse.

Oxygen - 1bar						
V [V]	I [mA]	P [mW]	D <sub>i</sub> [μm]	Vol [m <sup>3</sup> ]	n [mol]	
1.5	0.093	0.14	79.00	2.58E-13	1.20E-11	
1.6	0.148	0.24	54	8.24E-14	3.84E-12	
1.70	0.193	0.33	56.00	1.1E-13	5.01E-12	
1.80	0.193	0.35	59.00	1.08E-13	5.01E-12	
1.9	0.214	0.41	61	1.19E-13	5.53E-12	

As well as in the hydrogen case, the diameter corresponding to 1,5V is not following the projection of the other ideal diameters. In this it is bigger even than the diameter corresponding to 1,9V. This could give the reason to think that, for both gases, their bubble diameters would be smaller if 1,5V would be applied only 10ms, and most probably would follow the linear projection. Another aspect to be considered is that for ideal settings, the minimum required voltage for electrolysis of  $H_2$  and  $O_2$  is 1,48V. Below this value, no electrolysis is possible. Accounting for realistic losses, even the 1,5V might be too small to initiate the electrochemical processes. Figure 7.13 shows relationship between oxygen bubble ideal diameter and voltage, and the linear progression.

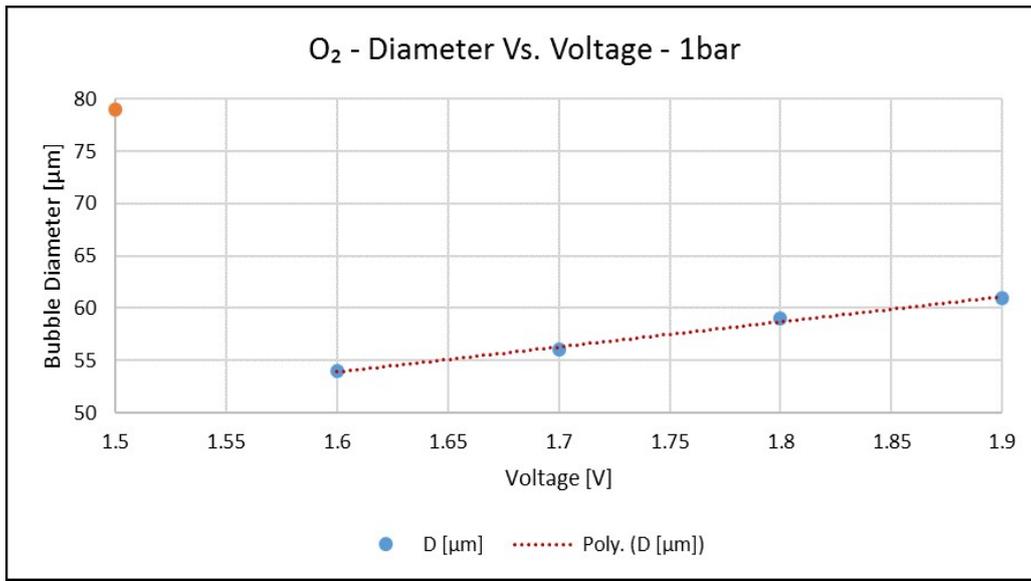


Figure 7.13: Diameter of one oxygen bubble per pulse vs. applied voltage.

In general, and regarding the ideal diameter, hydrogen bubbles present bigger ideal diameters than oxygen. According to the elementary equation of the electrolysis double amount of moles of hydrogen are produced than moles of oxygen for the same electrical signal and environmental conditions. This is reflected in tables 7.2 and 7.4.

By dividing equation 3.4 by 3.3, the relationship of hydrogen and oxygen moles is:

$$N_{H_2}/N_{O_2} = 2I_{H_2}/I_{O_2} \quad (7.2)$$

Equation 7.2 says the hydrogen moles production is double as oxygen, the current is equal for both gases. For 1.7V case, both gases have presented similar values of electrical current, 0.183mA and 0.165mA for hydrogen and oxygen correspondingly. Taking the rate of hydrogen and oxygen mole production, the result is nearly 2, in this case is 2.2.

If the 1.9V case is analyzed, the electrical current was higher when hydrogen was produced at the glass coated wire electrode. It was practically double than for oxygen, 0.416mA and 0.214mA. Thus, for the same applied voltage, hydrogen is presenting less resistance than oxygen, and consequently a higher current is obtained. For the same electrode configuration and same applied voltage oxygen has presented a higher resistance is produced at the glass coated wire electrode. It is interesting to observe that the electrical circuit presents different values depending on which electrode produces a specific gas. For 1.9V the rate of moles is nearly 4, in this case 3.9. Figure 7.14 shows the gases moles production, in dark blue spots the moles rate.

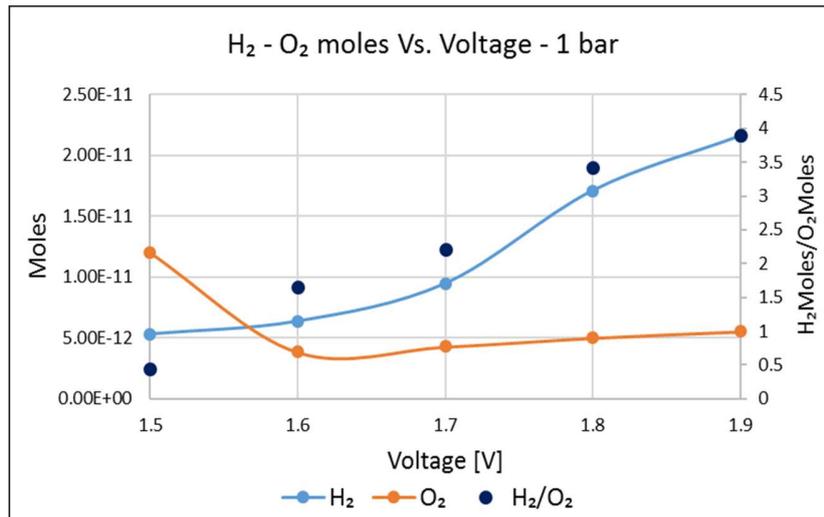


Figure 7.14: Hydrogen and Oxygen moles production vs. applied voltage.

A possible explanation of this is, that hydrogen is offering less resistance at higher voltages, and so current presents higher values. This could be explained by looking at the diameters values, which are smaller than the calculated ideal diameter, what is offering less resistance to the voltage.

However, the reason why hydrogen and oxygen are having this behavior cannot be explain. In principal, the applied forces or the saturation nearby the electrode could be some reasons.

Finally, by comparing the actual results with the previous results with bubble swarms, it can be seen for both gases, that the actual diameters are bigger. Moreover, the actual wideness of diameter distribution is more narrowed compare with the previous range, especially in the case of oxygen and hydrogen.

## 7.1.2 High pressure

In order to continue with the analysis, the results of the bubble diameters at high pressures are going to be presented. As expected, diameters decrease with the increasing pressure. However, for higher pressures, measurements were taken only applying 1.7V and 1.9V.

### 7.1.2.1 Hydrogen high pressure

As it was expected, taking into account tendencies from previous results [4], hydrogen diameter decreases and their distribution narrows with increasing pressures. Figure 7.15 shows the diameters frequency specified by the histogram bins. In this case 1.9V with a time pulse of 10ms were applied. Pressure of 1bar, 40bar and 180bar are presented.

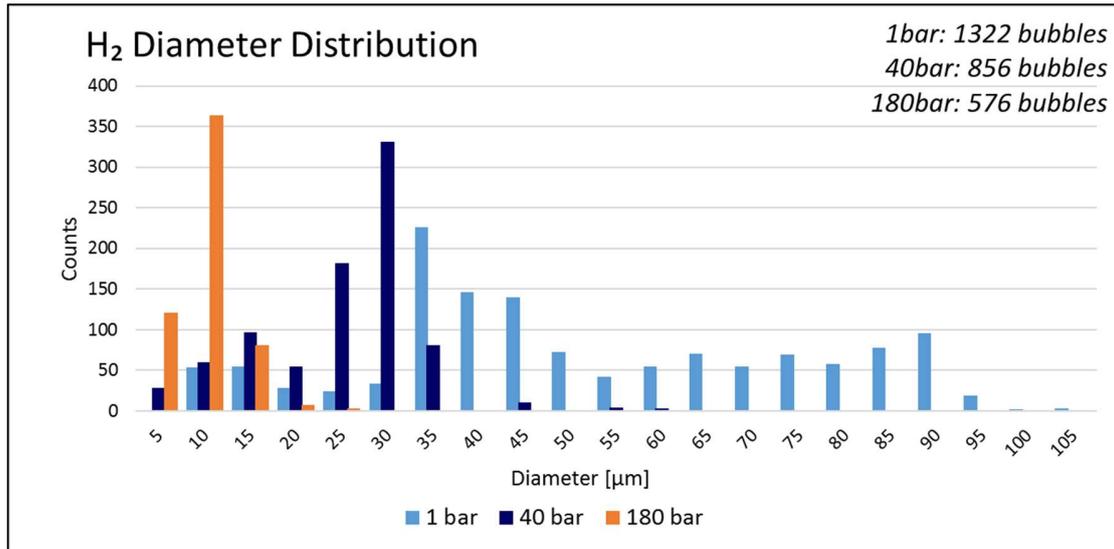


Figure 7.15: Hydrogen bubble diameter distribution – 1bar, 40bar, 180bar.

The mean diameter of each measurement are 36μm at 1bar, 26μm at 40bar and 13μm at 180bar, showing a decreasing tendency.

Moreover, the distribution at 1bar goes from 10μm to 105μm, while at 180bar the distribution range is from 5μm to 25μm, what shows clearly how the ranges are narrowing. Accordingly, the standard deviation decreases, supporting the previous observation, 22.9 was obtained for 1bar, 9.0 for 40bar and 3.1 for 180bar, meaning that diameters tend to show closer defined values. In table 7.5 and table 7.6, a summary of the bubble size distribution is presented for 1,7V and 1,9V.

Table 7.5: Representative diameter and STD – 1,7V, 10ms time pulse, 1010ms period.

H <sub>2</sub> - 1,7V		
Pressure [bar]	Diameter [μm]	STD
1	68.7	12.9
20	22.4	8.7
40	12.3	5.7
60	18.4	10.3
80	14.2	5.0
140	12.5	2.2
180	11.2	2.7

Table 7.6: Representative diameter and STD – 1,9V, 10ms time pulse, 710ms period.

H <sub>2</sub> - 1,9V		
Pressure [bar]	AV - D [μm]	STD
1	54.5	22.9
20	23.5	8.1
40	22.5	9.0
60	10.5	2.8
80	20.6	8.7
140	16.1	5.2
180	13.8	3.1

To have a clear overview of the diameter tendency, figure 7.16 is built with data in tables 7.5 and 7.6.

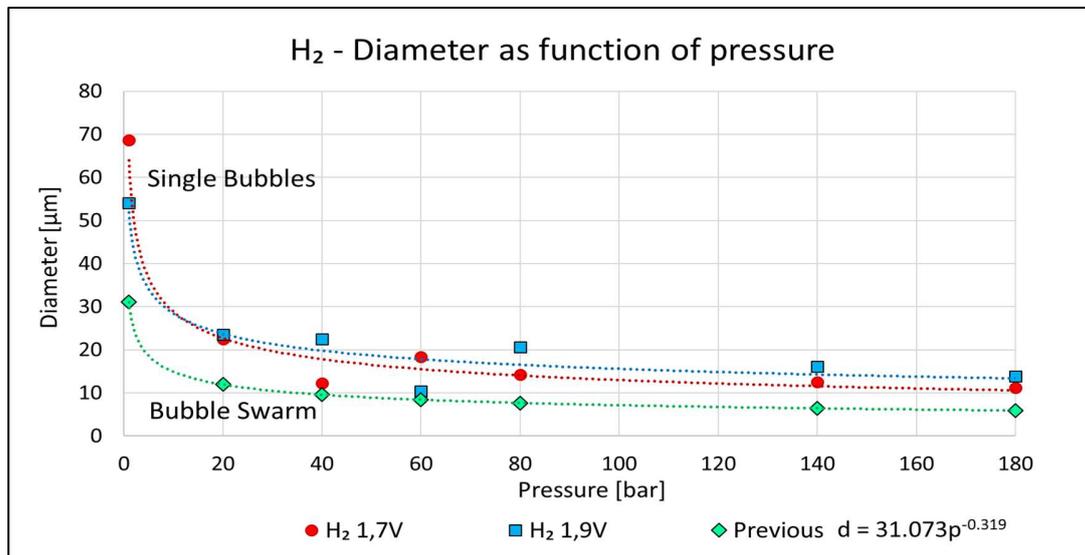


Figure 7.16: Hydrogen - Diameter as function of pressure

In figure 7.16, three curves are presented, both red and blue represent the actual measurements, the green diamonds mark results of Frey [4].

It can be seen that the tendency of 1,7V and 1,9V curves are similar with each other and with the curve obtained previously. Here, however, diameters were slightly bigger; what could be associated with the difference between the single bubble behavior and the bubble swarms. The need of a faster production of bubbles in the case of a swarm, could explain why more and smaller bubbles are produced.

Finally, it can be seen that for most of the measurements, the 1,9V curve (squares) shows slightly greater diameter values than the 1,7V curve (spheres).

### 7.1.2.2 Oxygen high pressure

Oxygen bubbles were similarly analyzed. Figure 7.17 presents the diameter distribution corresponding to 1bar, 60bar and 180bar. In the case of 1bar and 60bar, the input signal was of 1,9V with 10ms of time pulse and a period of 710ms. For 180bar measurements, 1,9V was applied.

Regarding the distribution wideness, a different behavior is observed in comparison with hydrogen. The wideness of the distribution is neither affected by the increasing pressure or the power supply. It seems that for each case an amplitude of approx. 20 $\mu$ m is maintained. What it means that oxygen has presented much more defined diameters.

Moreover, the number of bubbles are less than in the hydrogen case. Both observations could be explained by the same reason as for ambient pressure. The electrical resistance is greater for oxygen as bubbles are staying more time at the electrode tip, and then less oxygen per time is produced. Furthermore, the reason of the long residence time of bubbles could be the influence of the electrode material [10] and the glass coating, which affects the contact angle.

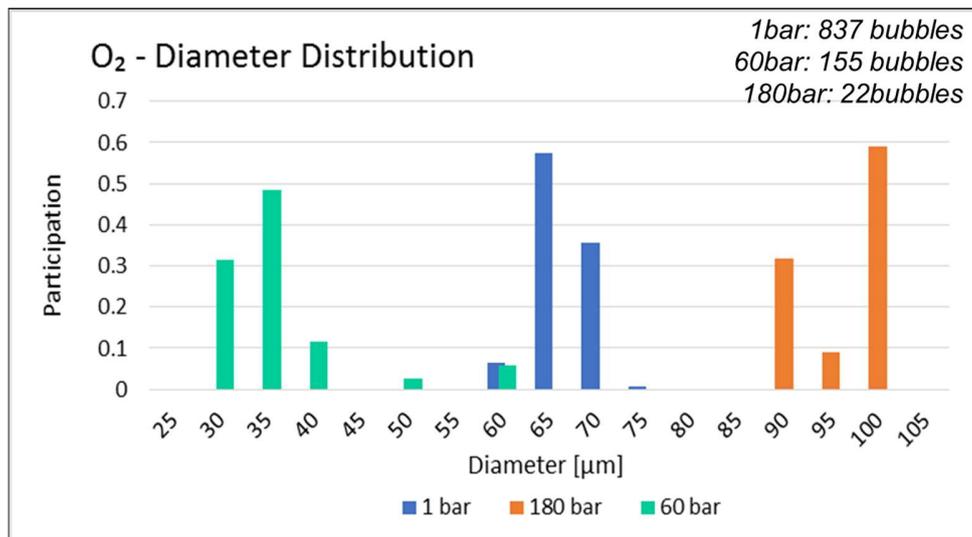


Figure 7.17: Oxygen bubble diameter distribution

By comparing results from 1bar and 60bar measurements, the tendency of the diameter to decrease with increasing pressure is again observed. This is not happening when comparing with 180bar. Potential reason for this is that, as mentioned previously, a different power supply was used. In this case more power input was registered, what has generated bigger bubbles. This also shows, how power supply influences the bubble behavior. In figure 7.18, the relation between bubble diameter and increasing pressure is presented.

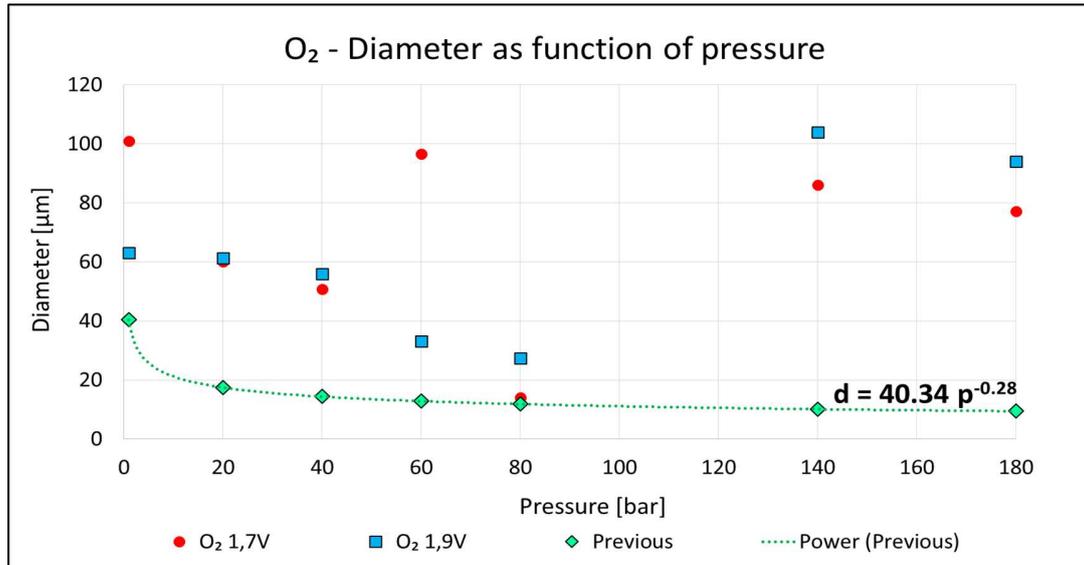


Figure 7.18: Oxygen - Diameter as function of pressure

Although oxygen does not show a clear tendency as hydrogen, for similar experimental settings diameters are decreasing with increasing pressure. In this case, diameters are also showing greater values than in [4]. The reason could be the same that was supported for hydrogen.

For 140bar, 180bar, and 1.7V at 60bar greater diameter values are evolving. This is due to the fact that in those measurements constant direct current was applied. The reason for using constant direct current was to increase the frequency of bubbles generation. It was observed that oxygen bubbles required more time to form when pulses were applied.

For the same pressures and in particular when continuous direct current was applied, diameter clearly increases with increasing voltage.

Again, it can be seen that the power supply is influencing the bubble sizes. Table 7.7 and 7.8 present the mean diameters, which values were well defined. This is due to the narrowed distribution that every case has presented.

Table 7.7: Representative diameter and STD – 1,7V, 10ms time pulse, 710ms period and D.C.

O <sub>2</sub> - 1,7V		
Pressure [bar]	Signal	Diameter [µm]
1	Pulse	100.9
20	Pulse	60.0
40	Pulse	50.8
60	D.C.	96.8
80	Pulse	14.1
140	D.C.	86.0
180	D.C.	77.1

Table 7.8: Representative diameter and STD – 1,9V, 10ms time pulse, 710ms period and D.C.

O <sub>2</sub> - 1,9V		
Pressure [bar]	Signal	Diameter [ $\mu\text{m}$ ]
1	Pulse	63.1
20	Pulse	61.3
40	Pulse	55.9
60	Pulse	33.6
80	Pulse	27.3
140	D.C.	103.9
180	D.C.	94.1

## 7.2 Rising Velocity

In this section the mean velocities of bubbles are presented. The rising velocity as function of diameter is analyzed and terminal velocity of the bubbles, following Stokes law, will be observed. The applied voltages have been 1,7V and 1,9V.

### 7.2.1 Atmospheric Pressure.

As for the bubble size investigations, measurements and results corresponding to 1bar are analyzed in more detail. Results corresponding to higher pressures will be presented in the following sections.

#### 7.2.1.1 Hydrogen

The distribution of the rising velocity are presented in figures 7.15 and 7.16.

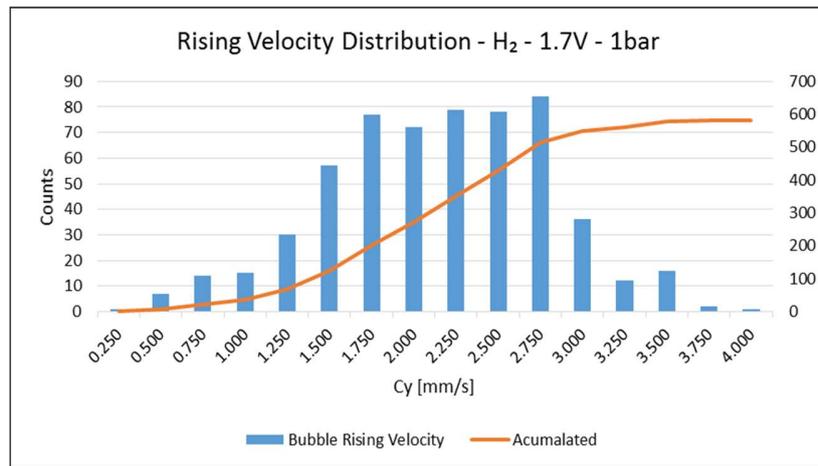


Figure 7.19: H<sub>2</sub> bubble rising velocity distribution – 1,7V – 1bar

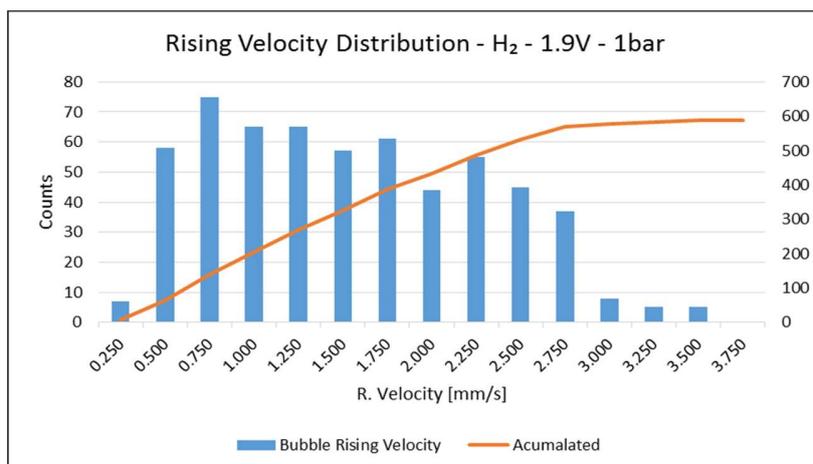


Figure 7.20: H<sub>2</sub> bubble rising velocity distribution – 1,9V – 1bar

Figures 7.19 and 7.20 show the velocities that were calculated and its frequency. By comparing them, it can be seen that for 1,9V the velocity distribution is wider than for 1,7V. This could be explained by the fact that for 1,9V, bubbles presented a wide range of diameter values. If the rising velocity is increasing with the diameter, then, this can explain why slower velocities have a high frequency for 1,9V, since smaller diameters have appeared more often when 1,9V were applied.

Moreover, the diameter size distribution for the 1,7V is much narrower, what would lead to the assumption that the velocity distribution should also be narrow. However, the distribution corresponding to 1,7V has a considerable range. The reason is that, the rising bubbles experience an acceleration, and so velocity will show increasing values for different positions further away from the electrode.

However, figures 7.15 and 7.16 do not show any relationship either with the bubbles diameter or with the position of the bubble.

Consequently, the rising velocity was investigated as function of the vertical position. For both cases, 1,7V and 1,9V, two different diameters were analyze. Figures 7.17 and 7.18 present the data and tendency lines correspondent to different bubbles of the same size.

The results show that bubbles are moving faster when they are far away from the electrode.

It is also observed that the rising velocity, in average, is higher for bigger diameters.

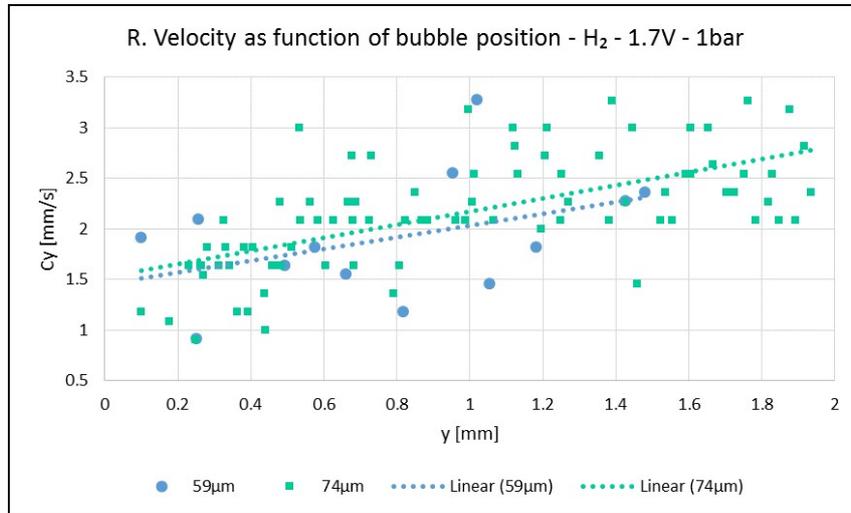


Figure 7.21: H<sub>2</sub> Data set and tendency lines of the rising vel. as function of vertical position of bubbles with diameters of 59µm and 74µm – 1.7V – 1bar.

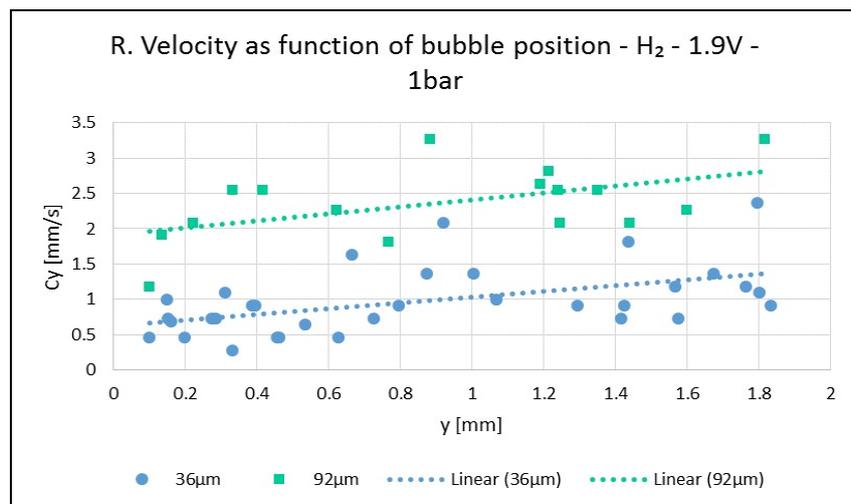


Figure 7.22: H<sub>2</sub> Data set and tendency lines of the rising vel. as function of vertical position of bubbles with diameters of 36µm and 92µm – 1.9V – 1bar.

Due to the greater diameter difference analyzed in Figure 7.22, the rising velocities also showed a larger difference than for the 1.7V case in figure 7.21.

So far, it has been observed that the rising velocity is influenced by the bubble diameter and that increases as the bubble moves away from the electrode. In order to get more into detail regarding the mentioned points, the rising velocity average per diameter was taken and the terminal velocity was observed.

Figure 7.23, was constructed in order to analyze the velocity as function of the diameter.

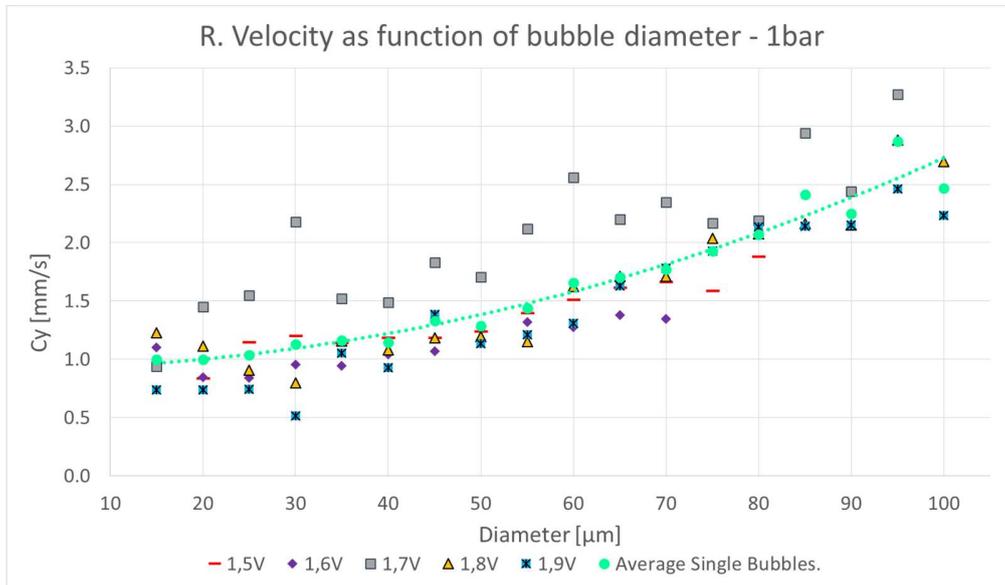


Figure 7.23: Hydrogen rising velocity average per diameter – All applied voltages – 1 bar.

The data of every applied voltage was filtered by diameter, then the average velocity was taken for each size, finally an average curve was build. In every case the tendency shows that the rising velocity increases with the increasing diameters. As this are average curves, there is no possible comparison with Stokes' Law.

Moreover, it can be seen, that the dataset corresponding to 1,7V is above the average trend line. This could be explained, by observing that this signal presents a greater frequency of bubble generation, bringing them closer to each other during the rising. This could be interpreted, as they are closer to the bubble swarm behavior, what increases the velocity value for each diameter.

Furthermore, some bubbles were study in particular in order to corroborate the predictions of the Stokes' Law. If the obtained velocity values are in the same order of the prediction, then this explains the acceleration that is already noticed. The analysis will be shown in the following section together with the high pressure results.

### 7.2.1.2 Oxygen

As for hydrogen, similar analysis of rising velocity of si oxygen performed. Figures 7.21, 7.22, 7.23 and 7.24 show the velocity distribution and the velocity as function of the position for 1,7V and 1,9V. The same tendencies are also the realised for hydrogen. The oxygen bubbles have shown a narrowed distribution, therefore velocities distributions are also narrowed.

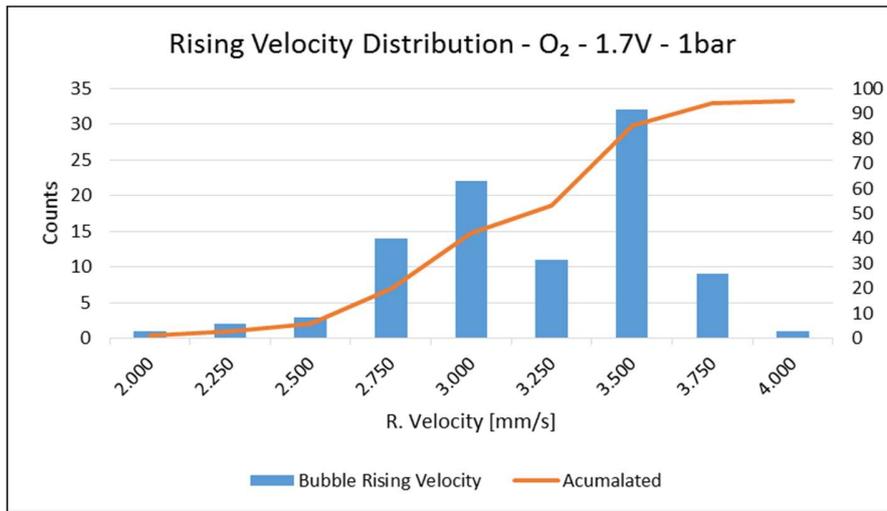


Figure 7.24: Oxygen rising velocity distribution – 1,7V – 1bar

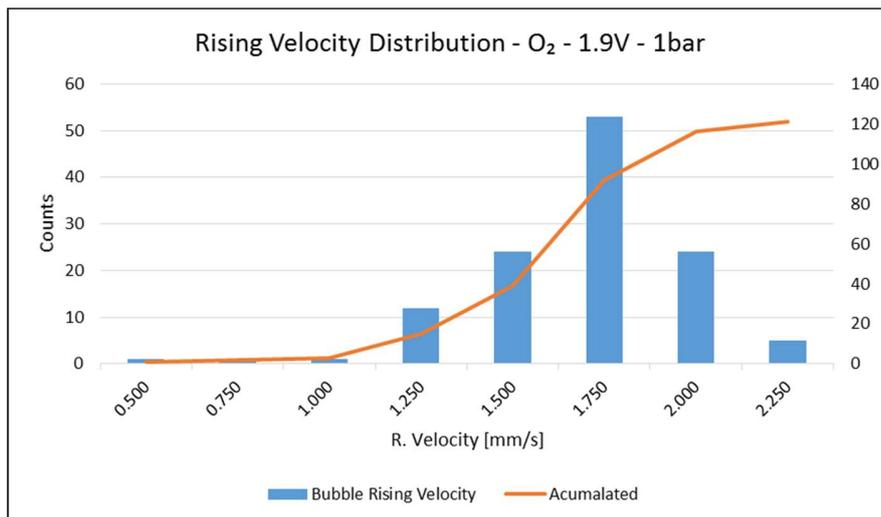


Figure 7.25: Oxygen rising velocity distribution – 1,9V – 1bar

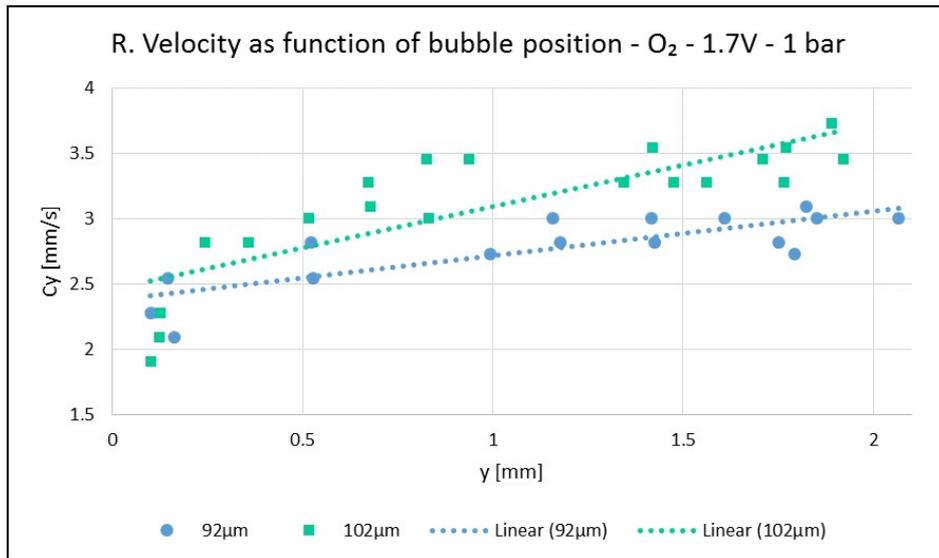


Figure 7.26: Figure 1.22: Data set and tendency lines of the rising vel. as function of vertical position for oxygen bubbles with diameters of 92µm and 102µm – 1.7V – 1bar.

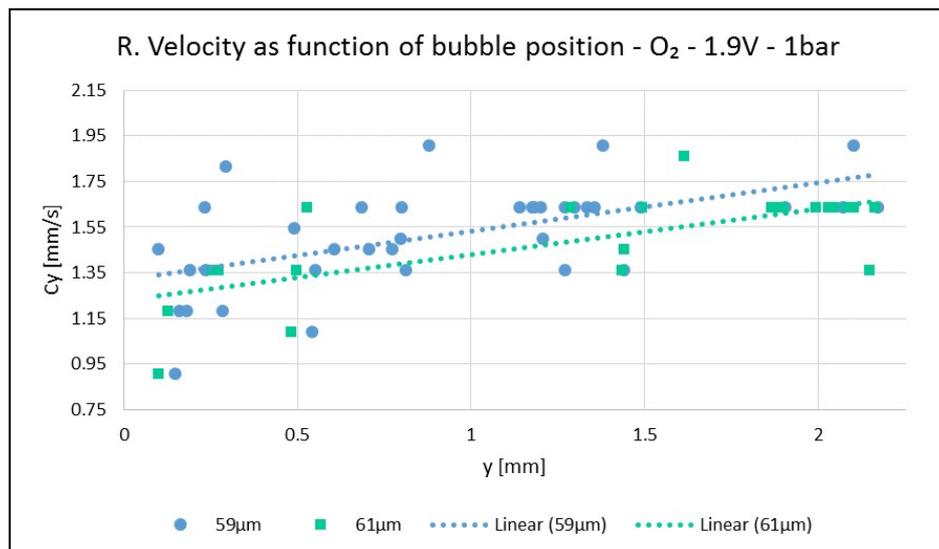


Figure 7.27: Data set and tendency lines of the rising vel. as function of vertical position for oxygen bubbles with diameters of 59µm and 61µm – 1.9V – 1bar.

In figure 7.27, it can be seen that the smaller diameter presents higher velocities. However, as they have closer values, the error may have strong influence in the calculations. The result shown in figure 7.26 maintain the tendency, where for greater diameter, higher velocities have to be expected.

Furthermore, the relation between oxygen bubbles diameters and velocities is show in figure 7.28. Again, it is observed that the rising velocity increases with the increasing diameters.

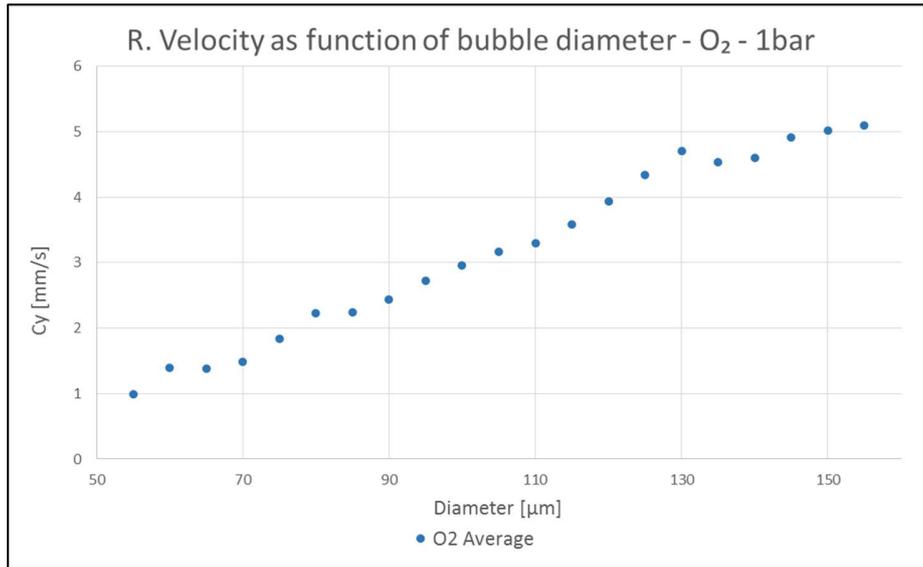


Figure 7.28: Oxygen rising velocity average per diameter – 1 bar.

## 7.2.2 High Pressure

In the current section the results from oxygen and hydrogen bubble velocities will be analyzed with respect to their dependence on pressure. Moreover the measurements and the Stokes' Law predictions will be compared and, finally, previous results and actual measurements will be compared.

At first, an overview of the velocities distribution is presented in figure 7.29 shows the results of hydrogen and oxygen bubble rising velocities for 1bar and 180bar.

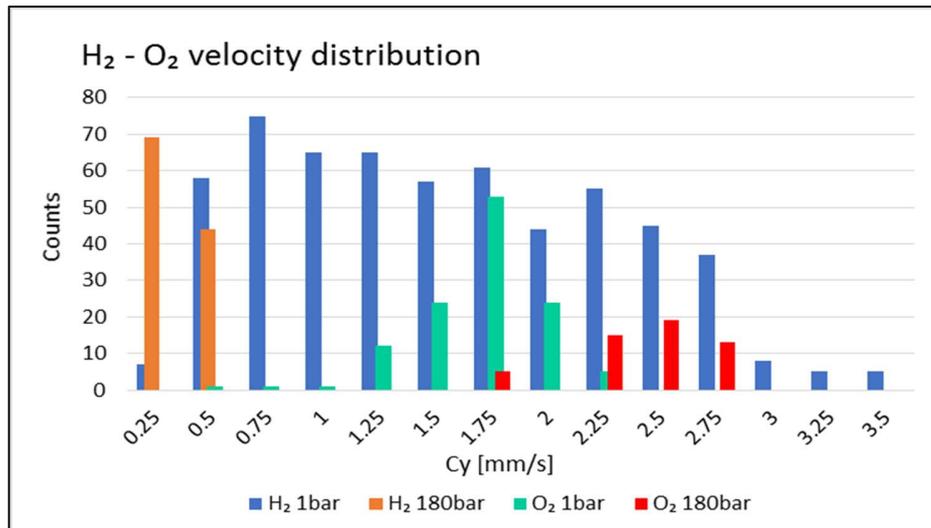


Figure 7.29: Oxygen and Hydrogen rising velocity distribution  
 $H_2/O_2$  at 1bar: 1.9V – 10ms time pulse – 710ms period  
 $H_2$  at 180bar: 1.9V – 10ms time pulse – 710ms period.  $O_2$  at 180bar: 1.9V D.C.

As explained before, at 1bar hydrogen shows a wider velocity distribution due to its wider diameter distribution. At 180bar the distribution narrows due to the fact that also bubble diameter decreases.

Moreover, when comparing hydrogen and oxygen at 1bar, the difference between their distribution's wide is clear, as it was mentioned before, this is due to the difference that both gases show also with respect to their size distributions.

The velocities of oxygen bubbles at 180bar have presented higher values because of their bigger diameter. Thus, the tendency of higher velocities for increasing diameters is once again corroborated. The velocity values show a narrowed distribution as consequence of the defined oxygen diameter at 180bar.

Showing rising velocities depending on pressure, Figures 7.30 and 7.31.

Starting with figure 7.30 for hydrogen, a clear tendency to decrease the rising velocity when pressure increases may be noticed. There is a higher decrease at the beginning and a lower slope at the end.

Moreover, a similarity with previous results can be observed. However, in this case the obtained velocities present lower values than in Frey's work [4]. It is shown that current measurements resulting in bigger diameters than before, what could lead to the conclusion that the velocities here should be higher than in the previous work. The explanation could be again the difference between the bubble swarm and the single bubble behavior, where the existence of a flow influences the swarm bubble velocities even when those bubbles present smaller diameters.

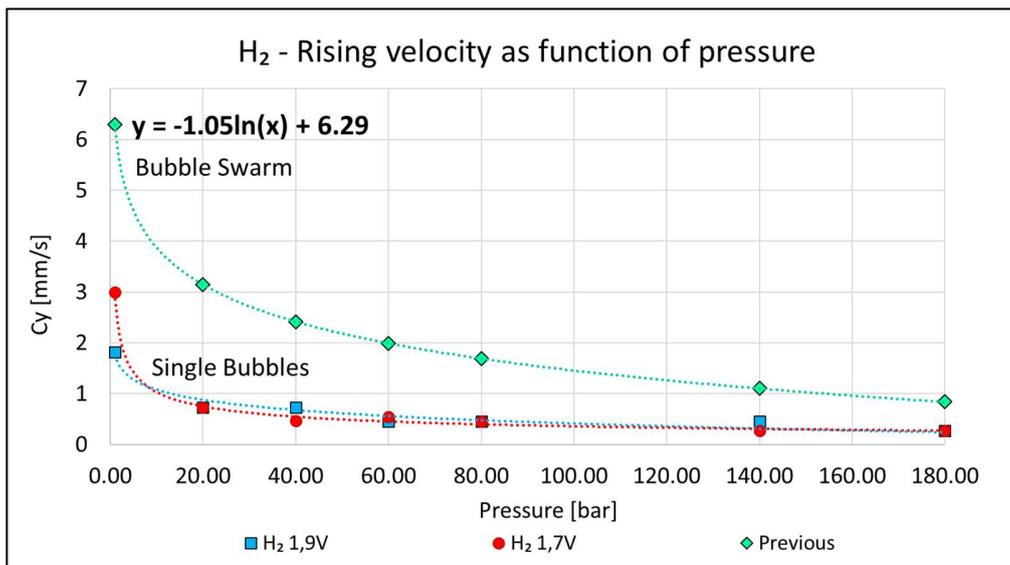


Figure 7.30: Hydrogen rising velocity as function of pressure 1,7V – 10ms time pulse – 1010ms period  
1,9V – 10ms time pulse – 710ms period

Moving on to oxygen, figure 7.31 shows the relationship between rising velocity and the increasing pressure. Once again the tendency of a decreasing velocity for an increasing pressure is obtained. However, as it happened in the diameter analysis, the tendency is not so clear, the reason could be the same as for the diameter. The fact that oxygen bubbles stick longer to the electrode generates more equally defined diameters.

The difference between current pulses and constant direct current is once again noticed. As it was presented before, the use of direct current have produced bubbles with bigger diameters than pulses and consequently higher velocities were calculated. This can be seen in figure 7.31. Furthermore, oxygen bubbles that were generated with direct current have shown, at the same pressure e.g. 180bar, higher velocities than in previous results. This again suggests the

explanation based on the bubble swarm and single bubble behavior. If single bubbles present diameters above a certain value, then their velocities would be higher than the swarm velocity, which is decreasing with the increasing pressure.

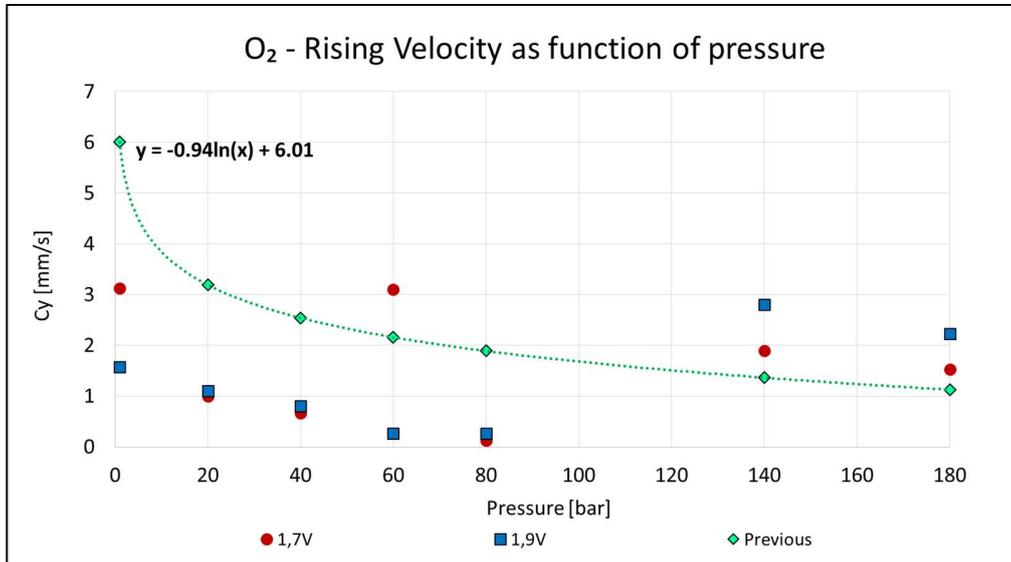


Figure 7.31: Oxygen rising velocity as function of pressure. 1,7V – 10ms time pulse – 1010ms period – D.C.  
1,9V – 10ms time pulse – 710ms period – D.C.

The present measurements and derived velocities are compared with Stokes' Law (See equations 2.12 and 2.13). The confirmation of the obtained velocities by the Stokes' Law prediction supports the idea of the single bubble behavior, even when, as it was shown, single bubble obtain higher velocities than in the case of the bubble swarm. In order to begin the analysis and show the results, figure 7.32 is presented.

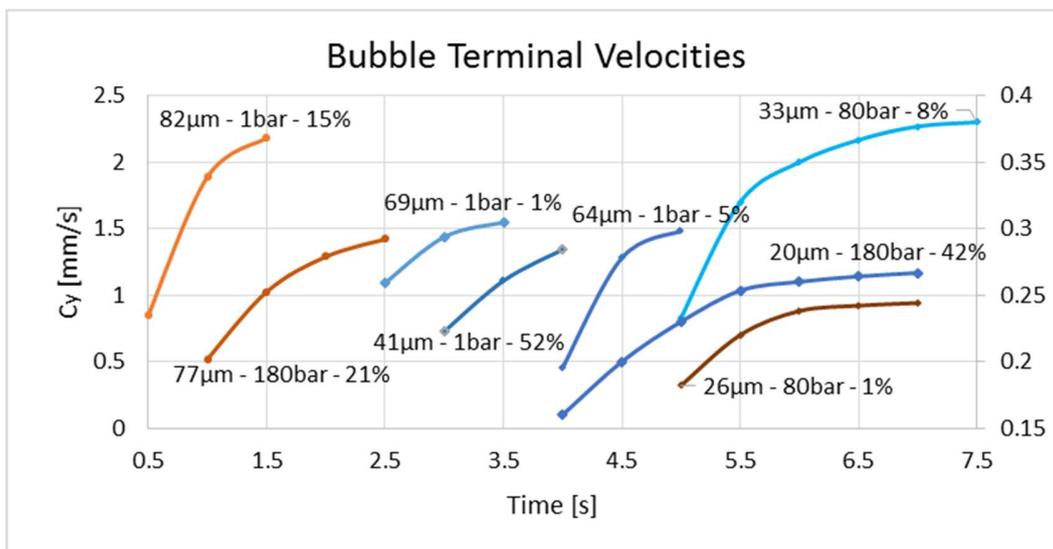


Figure 7.32: Hydrogen and oxygen bubble terminal velocities. Relative error is presented by comparing with Stokes' Law prediction.

Figure 7.32 was constructed by calculating the rising velocity for each corresponding time/position and comparing them to the Stoke's Law velocities, the bubble terminal velocity.

It can be noticed that the velocity curves over time correspond to bubbles that were taken from different series of experiment, even oxygen and hydrogen bubbles are shown in the same figure, the reason is that it was intended to show all the results together. What is important to see is that the first point always present a certain velocity and with the time axis it can be seen how much time it took to the bubble to reach the last calculated velocity. The three curves at the right side correspond to right vertical axis, which also measures speed in [mm/s]. The reason to separate them into a secondary axis was to have a better observation of the figure. Moreover, the curves are characterized by their diameter, the pressure at which measurement was taken and relative error in comparison with Stokes' Law calculation.

Table 7.9 shows the pressure and voltage at which measurements were taken, diameter of the bubbles, the maximum velocity value for all the curves, the Stokes' Law terminal velocity for the corresponding diameter and pressure and the relative error between both velocity values.

Table 7.9: Comparison between calculated velocities and Stokes prediction

H <sub>2</sub> /O <sub>2</sub> - Terminal Velocity						
Gas	p [bar]	Volt. [V]	Diameter [μm]	Cy [mm/s]	Stokes [mm/s]	E%
H2	1	1.5	69	1.79	1.82	1%
H2	1	1.5	64	1.49	1.56	5%
H2	1	1.5	41	1.35	0.64	52%
H2	80	1.7	33	0.38	0.41	8%
H2	180	1.9	20	0.26	0.15	42%
O2	1	1.5	82	2.18	2.56	15%
O2	80	1.9	26	0.24	0.23	1%
O2	180	1.7	77	1.42	1.79	21%

It can be seen that some calculations present a good approximation to the theoretical value. In those cases bubble were clearly detected as single bubbles. On the other hand, there are bubbles that are showing a bigger error. In the case of hydrogen, other bubbles influenced both examples with 41μm and 20μm, so it cannot be said that they represent a single bubble behavior, what could be the reason of the shown difference. In the case of oxygen, single bubbles were detected with diameter of 77μm and 82μm, obtaining higher rising velocity values. In both cases, the calculated velocities present an inferior value than the Stokes' prediction. Then, the reason of the difference could be that the bubbles need a longer distance to reach the Stokes' value as they are moving faster, what would happen only in a position above the visual inspection field.

Summing up, it is noticed that the velocity of the bubbles is increasing but not indefinitely. Instead, they reach a terminal velocity, which corresponds to the fluid dynamics theory, explained by the Stokes' Law. Although some of them are showing the expected results and reason were found to explain the cases where differences were found, only eight bubbles were analyzed in a rising distance of about 2mm, what implies that the analysis should be continued in order to support the results.

Finally, the rising velocity as function of the diameters is presented. Figure 7.33 presents the results of the actual measurements, representing the single bubble behavior, and the curves that were obtained by Frey in his work where swarms of bubbles were observed [4].

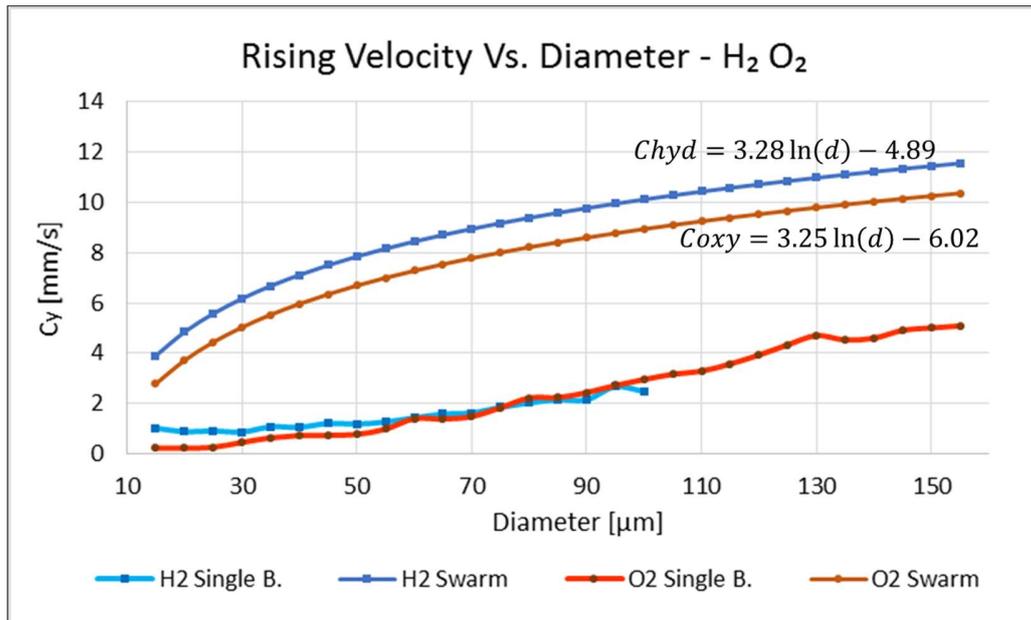


Figure 7.33: Hydrogen and Oxygen rising velocity as function of diameter. Comparison between previous and actual results.

Figure 7.33 is showing that, for the same diameters, a swarm of bubbles rise more rapidly than single bubbles. However, the condition of same diameter, do not assures same pressure. It was shown previously that, in the case of oxygen and for the same pressure, single bubbles could obtain greater diameters presenting higher speeds than the bubble swarm.

Moreover, in the previous work [4], hydrogen bubbles showed higer velocities than oxygen bubbles, but in the current measurements this difference is only clearly deteceted for smaller diameters.

## 7.3 Life time at free surface

In this section the last observation of the master thesis is presented. As it was mentioned before, this experiments were performed with a vertical arrangement in order to take imagenes from the plain view of the free surface. Measurements were taken only at atmospheric pressure, the top glass window was in total contact with the gas face and under this conditions it is not suggested to increase pressure.

For this point, only observation were made due to the difficulties that present the precise determination of the bubble diameters and the interpretation of the photos. Ranges of diameters will be related with ranges of the life time at the free surface, and some comment about what was observed will be done.

Figure 7.34 shows an example how lifetime of bubble was extrated from a sequence of images.

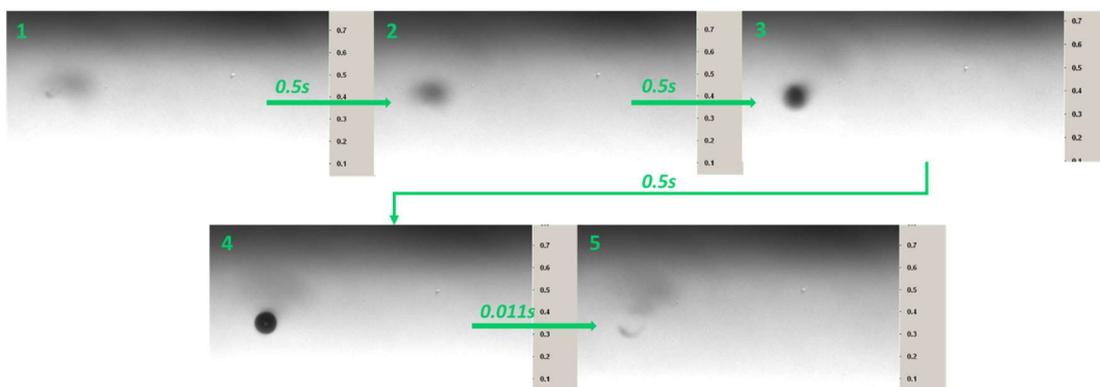


Figure 7.34: Sequence of 99 $\mu$ m diameter hydrogen bubble at the free surface  
1,9V – 10ms Pulse – 2010ms Period

In the secuence, it can be seen how the bubble is rising and reaching the free surface. Images from one to four present half a second between them, image five is the consective picture from image four. The last secuence shows how the bubbe goes through the free surface in 11ms.

### 7.3.1 Hydrogen

For hydrogen, two set of measurements were performed, the first one applying 2V and direct current, and the second one using 1,9V with 15ms of pulse time and 2010ms of period.

Beginning with the pulsed signal results, table 7.10 summarizes the observation.

Table 7.10: Hydrogen bubbles diameters and life time at free surface. 1,9V – 10ms Pulse – 2010ms Period

		H <sub>2</sub> life time at free surface - 1,9V - Pulse								
Diameter [ $\mu$ m]		15	23	28	31	36	38	56	86	99
Life time [s]		9	2	2	1.5	1.5	2	1	0.011	0.011

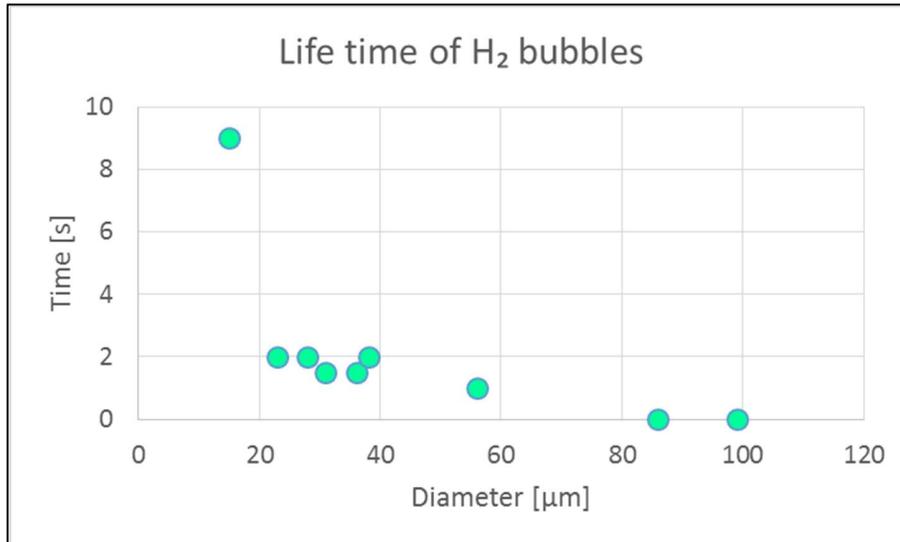


Figure 7.35: Lifetime of bubbles as function of diameter.

It can be observed in table 7.34, that bubbles with bigger diameters require less time to go through the free surface. Diameter have presented a range between  $15\mu\text{m}$  and  $99\mu\text{m}$ , which is consistent with the obtained distribution. Moreover, an example is presented, a sequence of images is shown in figure 7.35

Furthermore, below are presented the results corresponding to 2V and direct current. In this case diameters were bigger, most of the values were found between  $110\mu\text{m}$  and  $184\mu\text{m}$ , however there were cases where smaller bubbles have appeared.

Regarding the life time of the bubbles, by following the sequence of the consecutive pictures, 11ms of time delay between images, most of the cases have shown an instantaneous bursting at the free surface. It was also noticed, that some bubbles stayed some time, but not more than 0.5s.

In particular, the interaction of one bubble and dirt was detected, with the consequence that the bubble stayed at the free surface without bursting, 7s was the bubble at the free surface until it went out of the image frame.

Finally, sequences are presented in order to show what was observed. Figure 7.36 shows the sequence of two consecutive photos. In this case it shows the bursting of a bubble and how it has influenced the free surface. It is assumed that the other bubbles are not jet at the free surface because they are not showing any change in their position.

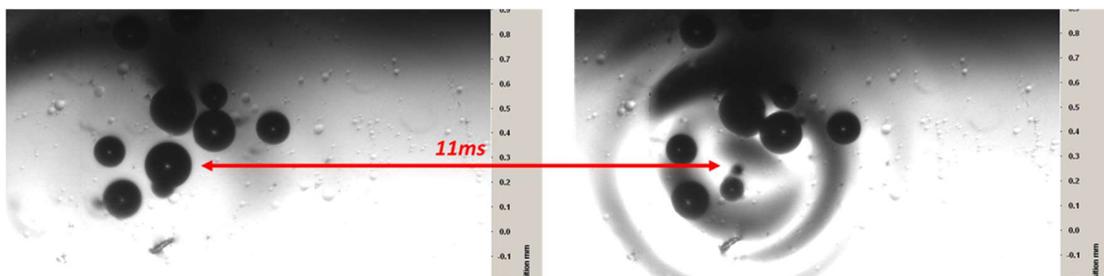


Figure 7.36: Bursting of  $140\mu\text{m}$  diameter hydrogen bubble

Figure 7.37 shows how two bubbles go through the free surface after 11ms. In this opportunity, the influence at the free surface is not noticed.

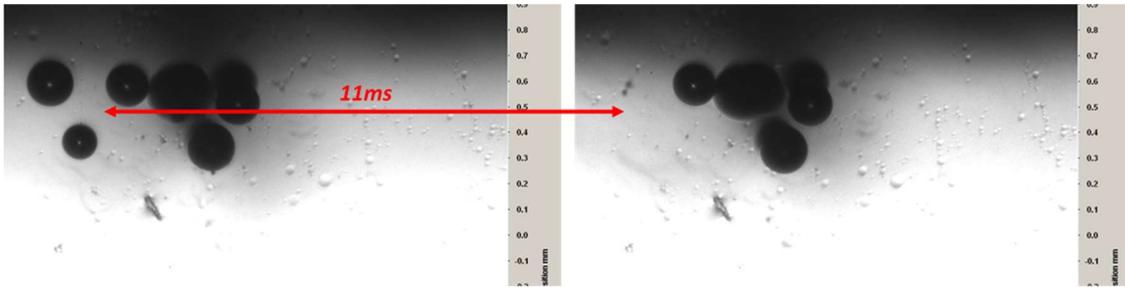


Figure 7.37: Bursting of 180 $\mu$ m and 110 $\mu$ m diameter hydrogen bubbles

It can be seen in figure 7.38, how bubbles that are apparently at the free surface do not burst during 11ms, but 0.5s after, the next image was taken, shows that those bubbles have gone through the free surface.

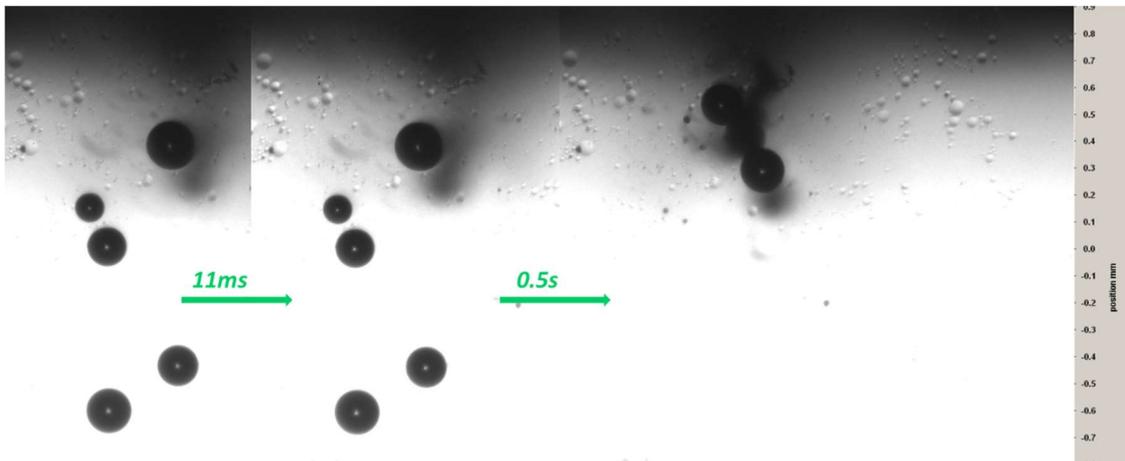


Figure 7.38: Bursting several hydrogen bubbles

It can be seen in figure 7.39, how some group of bubbles that are apparently at the free surface burst during and some of them stay there during the 11ms. In the next picture, which is not shown, no bubbles are observed, this represent 0.5s.

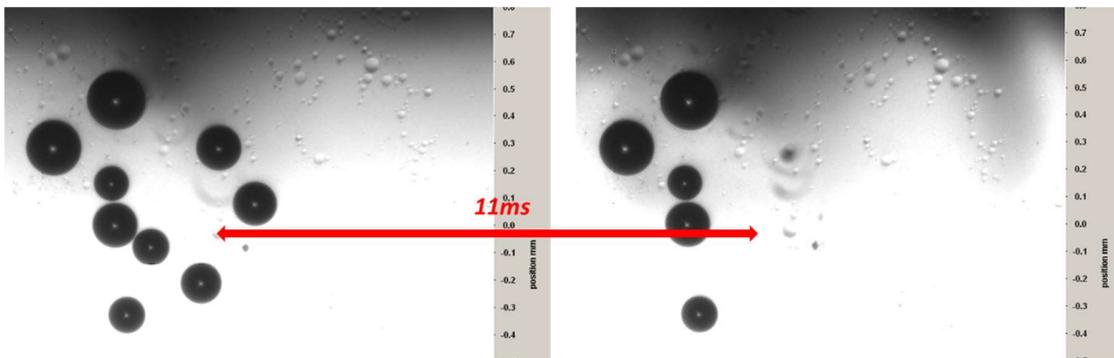


Figure 7.39: Bursting several hydrogen bubbles

### 7.3.2 Oxygen

In the case of oxygen only 2V and constant direct current were applied.

The diameters values were registered between 150 $\mu\text{m}$  and 270 $\mu\text{m}$ . Some group of bubbles appear to have an instantaneous bursting at the free surface. However, other observation could give the idea of bubbles staying some time at the interface. This time estimated at 0.5s. A sequence of images are presented below.

Figure 7.40 shows how a bubble of 270 $\mu\text{m}$  reaches the free surfaces and bursts 11ms thereafter.

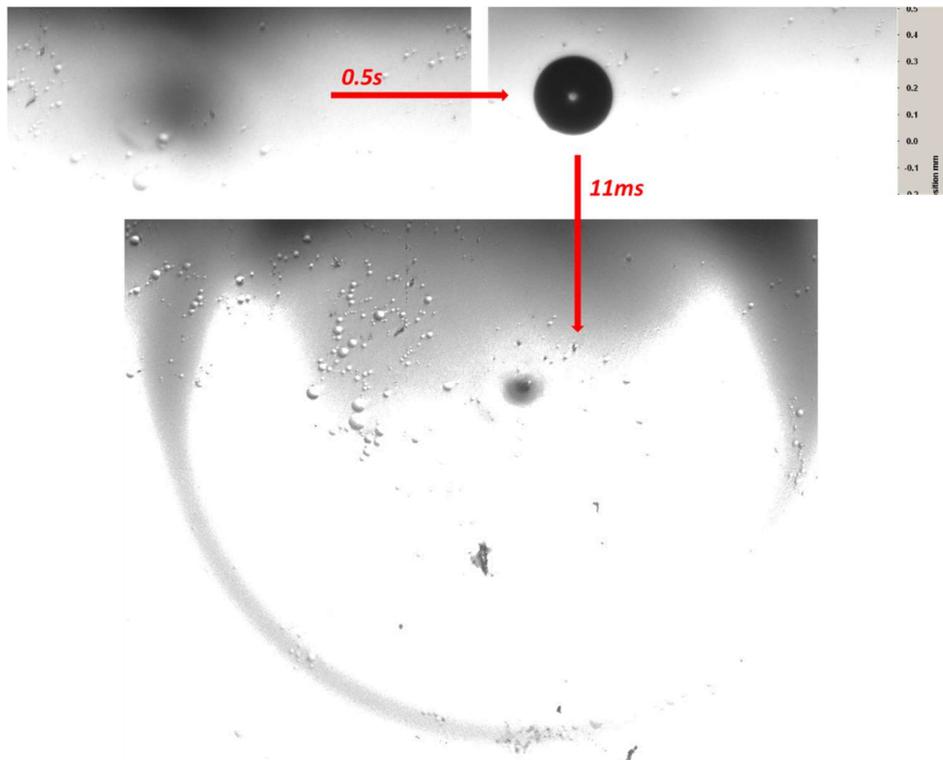


Figure 7.40: Bursting of a 270 $\mu\text{m}$  oxygen bubble.

A similar case is presented in Figure 7.41. Hier the moment where the bubble is passing through the free surface was detected. The bubble rises and reaches the surface during 0.5s, after 11ms it cannot be detected any more. This example could support the idea that in some cases the bursting is instantaneous.

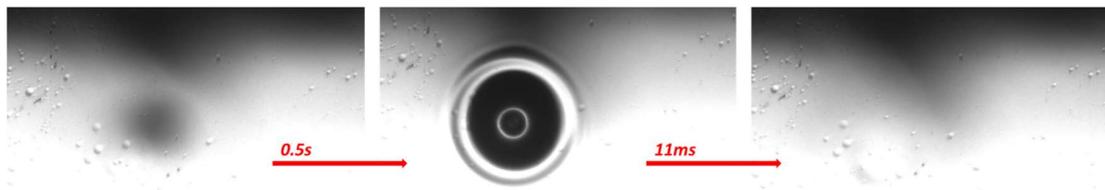


Figure 7.41: Oxygen bubble of 237 $\mu\text{m}$  going through the free surface

Following the previous examples, figure 7.42 shows how a oxygen bubble rises and bursts. The whole sequence takes about 0.5s. The right photo shows the disturbance at the free surface after their bursting of the bubble.

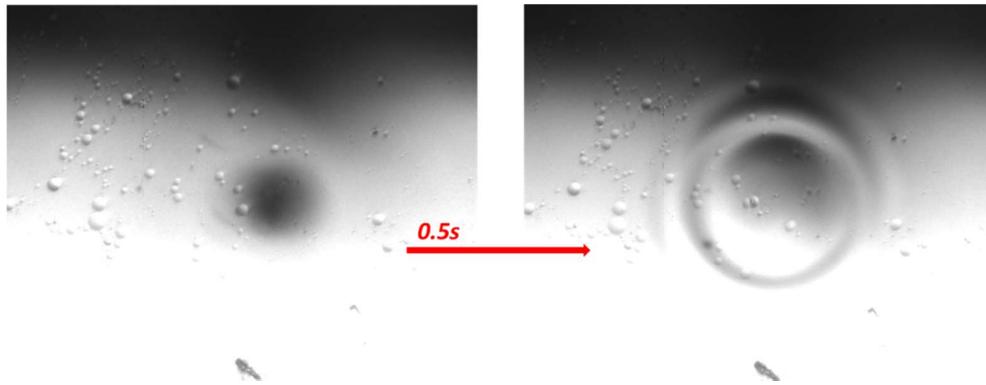


Figure 7.42: Oxygen bubble rises and bursts. Diameter could not be measured.

However, not all the cases have shown same tendency of instantaneous bursting as in the previous examples. In figure 7.43 a case is presented where the oxygen bubble has stayed at the free surface for more than 0.5s.

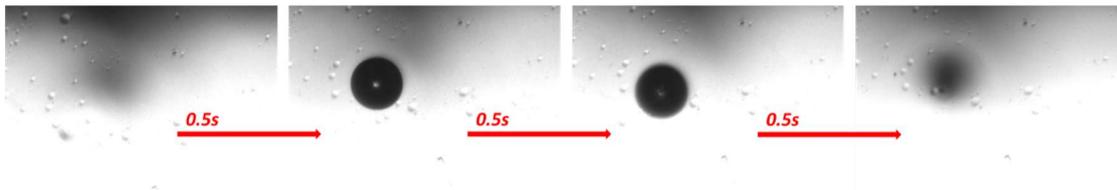


Figure 7.43: Oxygen bubble of 245µm diameter rises stays at free surface and bursts.

In summary, when hydrogen and oxygen bubbles were observed at the free surface at atmospheric pressure it was found, that the life time of the bubbles at the free surface depends on their diameter size. In the case of oxygen most of the observed bubbles have sustained no longer than 0.5s at the free surface. In the case of hydrogen the relation of life time and diameter was better defined. Foam was not detected in no case.



## 8 Summary

In this master thesis experiments were performed in the high-pressure optical alkaline experimental electrolyzer. The work was based on previous work of Frey [4], in which the electrolyzer set-up and electrode design promoted bubble swarms formation. In that case was studied the behavior of the bubble swarm regarding the bubble detachment diameter and their rising velocity.

This thesis is focused on the production and study of single bubbles. The results have shown differences in comparison with the bubble swarm behavior. In addition to the bubble detachment diameter and rising velocity characterization, observations were done of the bubbles lifetime at the free surface. This last series of experiments was performed only at atmospheric pressure.

In order to obtain single bubbles, a new electrode was designed and tested showing satisfactory results. Moreover, a pulsed signal was used, which also has contributed to this aim.

In order to operate the equipment under safe conditions, a safety analysis was performed regarding the hydrogen production, the KOH handling, and the high-pressure conditions. This analysis led to modifications of the equipment and to the final set-up of the experiments.

The pressure has been varied between 1bar and 180bar. A new power supply delivered electrical pulses of 1,7V and 1,9V with an active time of 10ms typically. Optical measurements of the generated bubbles were taken and then analyzed in order to obtain results.

To sum up, regarding the bubble size, results have confirmed that the bubble diameter decreases with increasing pressure. In the case of hydrogen, the detachment is instantaneous and the size distribution has shown a narrowing while pressure increases. On the other hand, oxygen bubbles stayed longer at the electrode tip and have shown narrowed distributions for all applied pressure levels. Reasons for this behavior could be the glass material covering the wire, which affects the contact angle, and the used electrical signal. In general, the actual results support the projections made in the previous work. However, different values were observed as single bubbles presented greater diameter than in the bubbles swarm. Finally, it was observed that for different voltages different diameters were obtained.

For the rising velocities, it was observed that it increases with the increasing diameters and decreases with the increasing pressure. Both gases have shown similar values for similar diameters. Still differences were detected especially for small diameters. The obtained velocities were compared with the Stokes' law prediction showing good approximations. Finally, a comparison was done with previous results, showing that the swarm of bubble presents higher velocities than single bubbles.

Finally, the observation of the bubbles' lifetime at the free surface has shown that the time the bubbles stays at the free surface increases with decreasing diameters. No foam was observed and it was also detected that impurities at the free surface affect the bubble bursting. For the observed diameters, it could be said that bursting tends to be instantaneous.

To conclude, in this master thesis the difference between the bubble swarm and single bubble behavior was successfully investigated. It was observed that applied electrical sources and material have considerable influenced on the bubbles behavior.



## 9 References

- [1] Dr.-Ing. Thomas Jordan, Skript zur Vorlesung über Wasserstofftechnologie, Version 2015.1, KIT, April 2015
- [2] [http://www.cac.com.ar/data/documentos/19\\_Ley%2027%20191.pdf](http://www.cac.com.ar/data/documentos/19_Ley%2027%20191.pdf)
- [3] [https://en.wikipedia.org/wiki/Renewable\\_energy\\_in\\_Germany](https://en.wikipedia.org/wiki/Renewable_energy_in_Germany)
- [4] F. Frey, Experimental set-up for bubble behavior in a high-pressure alkaline electrolyte, Master thesis, KIT - ITBA, Karlsruhe, 2016
- [5] S.K Mazloomi, Influencing factors of water electrolysis electrical efficiency, Renewable and Sustainable Energy Reviews, D. of Electrical and Electronic Engineering, University Putra Malaysia, Selangor, May 2012
- [6] Onda et.al. Prediction of production power for high-pressure hydrogen by high-pressure water electrolysis, Journal of Power Sources 132, 2004
- [7] R.L. LeRoy, C.T. Vower, D.J. LeRoy, J. Electrochem. Soc. 127 (1980), 1954
- [8] S.D. Lubetkin, The fundamentals of bubble evolution, Chemical Society Reviews, DowElenco Europe, Wantage U.K, Jan 1995
- [9] Dongke Zhang and Kai Zeng, Evaluating the behavior of electrolytic gas bubbles and their effect on the cell voltage in alkaline water electrolysis, ACS Publications, Centre for Energy (M473), University of Western Australia, Crawley, Australia, 2012
- [10] C.A.C. Sequeira, Physics of Electrolyte Gas Evolution, Sociedade Brasileira de Física, Department of chemical engineering, TU Lisbon, Lisbon, Portugal, Apr 2013
- [11] C.A. Ward, A. Balakrishnan, F.C. Hooper, Trans. ASME 92, 695, 1970
- [12] S.D. Lubetkin, Why is it much easier to nucleate gas bubbles than theory predicts?, American Chemical Society, Indiana, 2003
- [13] P.J. Sides, Ph.D. thesis, University of California, CA - USA, 1981
- [14] L.E. Scrivens, Chem. Eng. Sci. , 1959, 10, 1
- [15] B.Kabanov, A. Frumkin, Z. Phys. Chem. 165, 433, 1933
- [16] E.L. Littauer, U.S. Patent 3, 880,721, 1975
- [17] Muzhong Shen, A concise model for evaluating water electrolysis, Paper, Department of Mechanical & Design Engineering, University of Portsmouth, Portsmouth PO1 3DJ, UK, Dic. 2010
- [18] LaVision Gmbh, SizingMaster Shadow, Product-Manual - 1003014, Goettingen Germany, Nov. 2007
- [19] General Safety Regulation – KIT Campus North, Karlsruhe Institute for Technology, July 2015.
- [20] Y. N. SHEBEKO ET AL; Burning Velocities and Flammability Limits of Gaseous Mixtures at Elevated Temperatures and Pressures, Institute for Fire Protection Balashiha-3, Moscow Region, 143900, Russia, 1994

- [21] Schroeder, V.: Explosionsgrenzen von Wasserstoff und Wasserstoff/Methan-Gemischen, BAM Research Report No. 253, NW-Verlag, Bremerhaven, 2003
- [22] IMAGEJ, Particle Analysis, Online Manual – Section 5.1.1.1, [https://imagej.net/Particle\\_Analysis](https://imagej.net/Particle_Analysis), March 2017



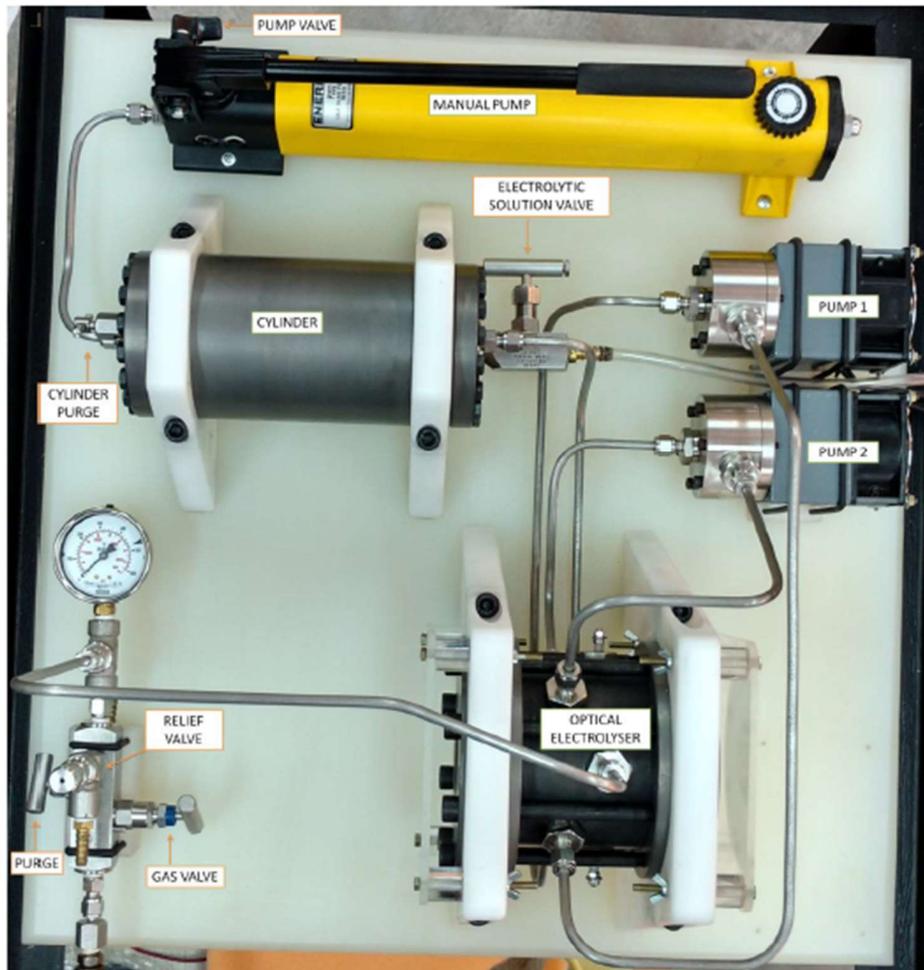


# A

## High-Pressure Optical Electrolyser STANDARD OPERATION PROCEDURE



## High Pressure Optical Electrolyser STANDARD OPERACION PROCEDURE



### Device Description:

The 8 port optical cylinder allows electric and hydraulic connections. Connectors are provided to meet the different requirements.

The tank configuration 1 components are two caps with glass viewers together with the set of M10x150 bolts and the 210 bar relief valve. This configuration must be used with pressures of up to 200 bar.

The tank configuration 2 components are two caps with glass viewers together with the set of M12x150 bolts and the 500 bar relief valve. This configuration must be used with pressures of up to 450 bar. When this configuration is adopted, the recirculation pumps must not be connected.

### Tank Configuration changing procedure:

Make sure that the chamber is empty, without pressure (see D1/D2) and that the electrodes are unplugged. Remove the safety acrylic glass and disconnect all the tube-connectors and the electrode wires. Loosen the tank bolts (without taking them out) before loosening the frame bolts.

Remove the upper frame of the supporting structure and take the tank into a safe and clean table. With the bolts heads facing the roof, loosen them and take them out. Change carefully the caps, making sure that all the bolts are tightened in small adjusting steps one bolt after the other until the metal contact between the cylinder and the caps is sure. Put the tank again into the frame and place the tubing connectors or caps in the tank. **Make sure that the pumps are not linked to the tank if the configuration 2 is adopted.**

Once the tank and the tubing are placed, tighten the frame. Finally, change the relief valve according to the configuration used.

#### A. Required protection equipment.

- Ocular protection during experimentation is required.
- Use gloves and overall for handling the electrolytic solution.

#### B. Required special supplies.

- 1- Electrolytic solution.
- 2- Nitrogen tank.
- 3- 900 cm<sup>3</sup> of hydraulic oil.

#### C. System pressurization

- 1- Charge pump with 900 cm<sup>3</sup> of hydraulic oil.
- 2- Retraction of piston: Verify that the purge valve, the electrolytic solution valve and the gas valve are closed and that the pump valve is open. Next open the nitrogen tank tap, previously connected, and control the flow of gas, using the gas valve, until the flow stops, ensuring a complete retraction of the piston. Finally close the gas valve and release the chamber pressure using the purge valve; close the purge valve.
- 3- Electrolytic solution fill: Open the electrolytic solution valve and pour the required amount of solution using a funnel (see the annexed table); close the valve.
- 4- Open the gas valve until the required initial pressure is reached; close the valve and the nitrogen tank tap.
- 5- Close the pump valve and make sure that the pump cap is in venting position. Finally pump until the required pressure is reached.

#### D1. System depressurization (electrolytic solution volume unchanged)

- 1- Open the pump valve partially until the pressure of the hydraulic oil is relieved (avoid opening abruptly), close the pump valve.
- 2- Open the purge valve until the pressure of the chamber is completely relieved (according to the manometer lecture); close the purge valve.

#### D2. Despressurization with electrolytic solution emptying.

- 1- Open the pump valve partially until the pressure of the hydraulic oil is relieved (avoid opening abruptly), close the pump valve.
- 2- Open the purge valve until a pressure of 10 to 20 bar is reached; close the purge valve.
- 3- Carefully open the electrolytic solution valve to empty the required amount of electrolytic solution (do not open the valve abruptly to avoid splatter of the solution); close valve.

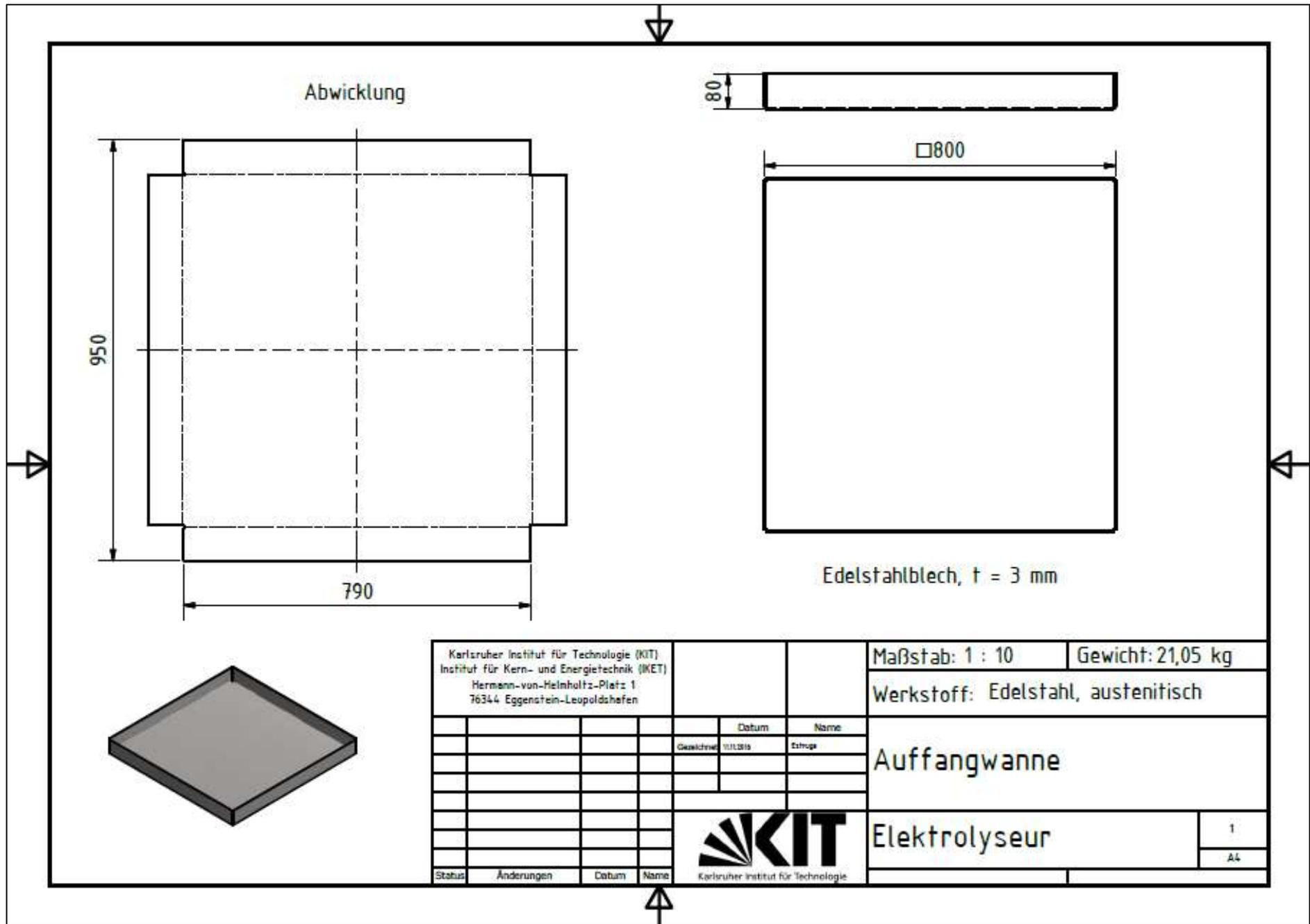
# B

## Drawings









Karlsruher Institut für Technologie (KIT) Institut für Kern- und Energietechnik (KET) Hermann-von-Helmholtz-Platz 1 76344 Eggenstein-Leopoldshafen					Maßstab: 1 : 10	Gewicht: 21,05 kg
					Werkstoff: Edelstahl, austenitisch	
			Datum	Name	Auffangwanne	
			Gezeichnet	Gezeichnet		
					Elektrolyseur	
Status	Änderungen	Datum	Name			1
						A4





# C

## Safety Analysis



**Hazard assessment**

# **High Pressure Electrolyzer**

**At IKET**

**Pablo José María Estruga**

**Version 1.0**

**December 2016**



## Table of Contents

<b>1</b>	<b>General safety regulations of KIT</b>	<b>91</b>
<b>2</b>	<b>Definition of responsibility areas</b>	<b>92</b>
<b>3</b>	<b>Task and function plan in security responsibility</b>	<b>93</b>
3.1	Institute leader	93
3.2	Experimental Director	93
3.3	Operational officer	93
3.4	Security officer	93
3.5	Specialist for work safety	94
3.6	Operation technicians and maintenance personnel	94
<b>4</b>	<b>Hazard assessment</b>	<b>95</b>
4.1	Preparation	96
4.2	Implementation	99
4.3	Conclusion/Post-Procedure	103
4.4	Maintenance Service	108
<b>5</b>	<b>Special safety rules</b>	<b>112</b>
<b>6</b>	<b>Exposure Areas</b>	<b>112</b>
<b>7</b>	<b>Instruction for guests</b>	<b>112</b>
<b>Appendix A</b>		<b>113</b>
A-1	Site plan containing laser laboratory with HPE	115
A-2	Description of high pressure electrolyzer	115
A-3	List of first aids responsables	118
A-4	Protocol on the instruction for guest scientists and third-party personnel	119
A-5	Checklist for the experiments	122
A-6	List of responsibilities	123
<b>Appendix B</b>		<b>125</b>
B-1	Nitrogen Safety Data Sheet	127
B-2	Potassium Hydroxide solution (KOH) safety data sheet	137
B-3	Electrolyzer	145
<b>Appendix C</b>		<b>147</b>
C-1	Description of experiments	149
C-2	Checklist for the experiments in HPE at KIT	150

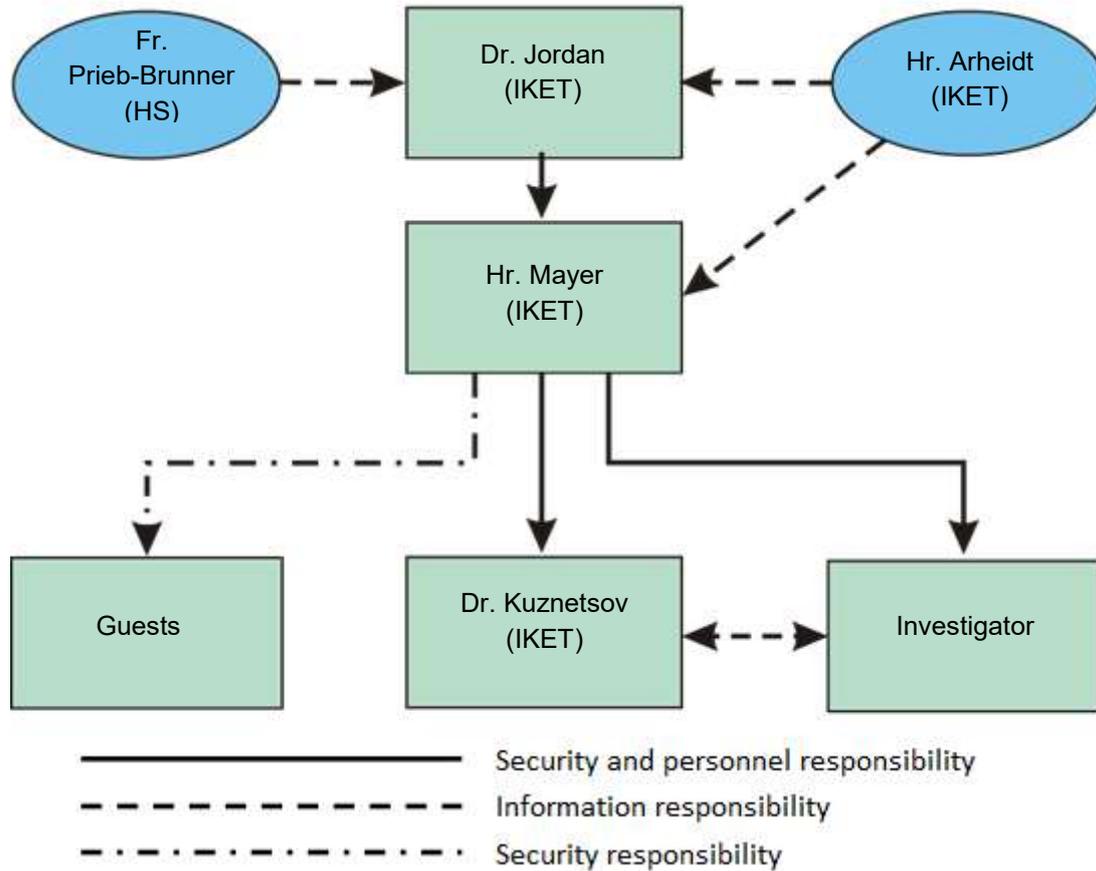
### 1 General safety regulations of KIT

KIT general safety regulation (version 07.2014) is the base for safety considerations. If nothing else is regulated for individual cases within this report, the rules described there are to be applied. In addition, the applicable laws regarding occupational health and safety, as well as the accident prevention regulations of the **Badische Unfallkasse** as an accident insurance institution (**Berufsgenossenschaft**) of the KIT apply.

## 2 Definition of responsibility areas

The areas of responsibility are defined as follows. In the case of changes in the personnel, modifications must be applied by the responsible trial manager or the institute manager.

### Responsibility areas for occupational health and safety:



The overall responsibility is of Prof. Dr. Schulenberg.

# Task and function plan in security responsibility

## 2.1 Institute leader

- Overall responsibility for occupational health and safety.

## 2.2 Experimental Director

- Elaboration, supplementation and adaptation of basic rules for experiments in HPE.
- Definition of responsibilities.
- Approval and coordination of the work that has to be carried out.
- Implementation of necessary measures from proposals in order to improve safety.
- Securement of hazard barriers.

## 2.3 Operational officer

- In security questions, the deputy of the trial leader.
- Check and verify compliance with the safety program.
- Check compliance with safety and accident prevention regulations.
- Control of the use of necessary personal protective equipment.
- Check for safety-related behavior.
- Execution control with regard to arranged measures.
- Collaboration in the preparation of hazard analyzes for hazard areas.
- Check the order and cleanliness of the test facility.
- Define measurements for exposure areas. Labeling exposure areas.

## 2.4 Security officer

- Support, advice and information of the trial leader and his deputy.
- Check and verify compliance with the safety program.

- Specialized and specific training of employees and guests.
- Recommendations and deadlines for the elimination of hazardous situations.
- Check compliance with the safety regulations.
- Control that necessary personal protective equipment is used.
- Check for safety-related behavior.
- Collaboration in the preparation of hazard analyzes for hazardous areas.
- Derive measures from results and controls.

## **2.5 Specialist for work safety**

- Establishment of priorities and fulfillment of the safety program.
- Coordination of the safety program, the supervisory authorities, the labor security office, the medical department and the works council.
- Coordination and support for the implementation of the security program.
- Supporting the trial leader by writing the draft for basic rules.
- Information and advice during the implementation of the safety program.
- General instruction of employees and guests.
- Saving and testing of safety-relevant protocols.
- Coordination in the preparation of hazard analyzes for hazard areas.

## **2.6 Operation technicians and maintenance personnel**

- Realization and implementation of the safety program in its own area of activity.
- Implementation of the measures ordered by the trial managers and the operational officers.
- Eliminate deficiencies in own area.
- Information and suggestions for measures to identify potential hazards to the trial manager and the operational staff.

# 3 Hazard assessment

Hazard analysis according to §5 Occupational Health and Safety Act (Och&SAct)

Date: \_\_\_\_\_

The hazard assessment is divided into:

- 4.1 Preparation
- 4.2 Implementation
- 4.3 Conclusion/Post-Procedure
- 4.4 Maintenance Service

KIT

Institut für Kern- und Energietechnik

Herrmann-von-Helmholtz-Platz 1

76344 Eggenstein-Leopoldshafen

Validation and responsible:

The risk assessment was conducted by:

The following were involved in the risk assessment:

The hazard analysis was discussed with:

## 3.1 Preparation

Nr.	Possible hazards / loads	Adequate measures	Measures (technical-organizational-personal) comments to implement measures	Consultancy requirements	Implementation Until/By	Effectiveness Effective/When
<b>1</b>	<b>Mechanical hazards</b>					
<b>1.1</b>	<b>Unprotected moving parts</b>					
<b>1.2</b>	<b>Parts with hazardous surfaces</b>					
	Sharpened electrode tips	Yes	Tips and electrodes should be stored in suitable box.	No	Realized	Yes
<b>1.3</b>	<b>Moving means of transport, moving equipment</b>					
<b>1.4</b>	<b>Uncontrolled moving parts</b>					
<b>1.5</b>	<b>Fall on the plane, slipping, stumbling, kinking, failure (work and traffic areas)</b>					
<b>1.6</b>	<b>Fall</b>					
<b>2</b>	<b>Electrical hazards</b>					
<b>2.1</b>	<b>Dangerous body currents circulation</b>					
<b>2.2</b>	<b>Electric arcs</b>					
<b>3</b>	<b>Hazardous substances</b>					
<b>3.1</b>	<b>Gases</b>					
	Nitrogen inhalation in very high concentrations	Yes	Follow the electrolyzer filling procedure to avoid leakages. In case of N <sub>2</sub> release, ventilate the laboratory.	No	Realized	Yes
<b>3.2</b>	<b>Vapors</b>					
<b>3.3</b>	<b>Aerosols</b>					
<b>3.4</b>	<b>Liquids</b>					
	KOH solution, leakages	Yes	For preparation of the solution follow manufacturer instructions and good practices, use gloves and glasses.	No	Realized	Yes
<b>3.5</b>	<b>Solids</b>					
<b>3.6</b>	<b>Continuous reactions</b>					

<b>3.7</b>	<b>Dust</b>					
<b>4</b>	<b>Biological hazards</b>					
<b>4.1</b>	<b>Infection by microorganisms, viruses, or biological agents</b>					
<b>4.2</b>	<b>Genetically modified organisms (GMOs)</b>					
<b>4.3</b>	<b>Allergens and toxic substances of microorganisms, etc.</b>					
<b>5</b>	<b>Fire and explosions Risks</b>					
<b>5.1</b>	<b>Fire hazard due to solids, liquids, gases</b>					
<b>5.2</b>	<b>Explosive atmosphere</b>					
<b>5.3</b>	<b>Explosives</b>					
<b>5.4</b>	<b>Electrostatic charge</b>					
<b>6</b>	<b>Thermal hazards</b>					
<b>6.1</b>	<b>Contact with hot media</b>					
<b>6.2</b>	<b>Contact with cold media</b>					
<b>7</b>	<b>Hazards due to special physical effects</b>					
<b>7.1</b>	<b>Noise</b>					
<b>7.2</b>	<b>Ultrasound, infrasound</b>					
<b>7.3</b>	<b>Whole body vibrations</b>					
<b>7.4</b>	<b>Hand-arm vibrations</b>					
<b>7.5</b>	<b>Non-ionizing radiation</b>					
<b>7.6</b>	<b>Ionizing radiation</b>					
<b>7.7</b>	<b>Electromagnetic fields</b>					
<b>7.8</b>	<b>Work in underpressure or overpressure</b>					
	Gas and liquid at high pressure	Yes	Look for damaged parts (connections, tubs). Check proper functioning of pressure gauge. Follow pressurization instructions and good practices.	No	Realized	Yes
<b>7.9</b>	<b>Danger of drowning</b>					
<b>8</b>	<b>Exposure to working environment</b>					

<b>8.1</b>	<b>Climate</b>					
<b>8.2</b>	<b>Lighting</b>					
<b>8.3</b>	<b>Space requirements / traffic routes</b>					
	Transportation and installation of electrolyzer	Yes	Make sure the electrolyzer is depressurized before transportation. Clear the path from one laboratory to another. Make sure, that there is enough space to mount all the needed equipment (electrolyzer, power source, computer, laser, camera).	No	Realized	Yes
<b>9</b>	<b>Physical stress / workload</b>					
<b>9.1</b>	<b>Heavy dynamic work</b>					
<b>9.1.1</b>	<b>Lifting and carrying heavy loads</b>					
	Electrolyzer and needed equipment	Yes	Make sure to use the proper transportation means. Electrolyzer must be carried at least by two persons.	No	Realized	Yes
<b>9.2</b>	<b>One-sided dynamic work</b>					
<b>9.3</b>	<b>Posture / holding work</b>					
<b>9.4</b>	<b>Combination of static and dynamic work</b>					
<b>10</b>	<b>Perception and manageability</b>					
<b>10.1</b>	<b>Information photographing</b>					
<b>10.2</b>	<b>Scope of perception</b>					
<b>10.3</b>	<b>Difficult handling of work equipment</b>					
<b>11</b>	<b>Other hazards</b>					
<b>11.1</b>	<b>Unsuitable personal protective equipment</b>					
<b>11.2</b>	<b>Skin strain</b>					
	Contamination of hands during assembly work	Yes	Clean contaminated skin, skin protection plan is hanged. Wear protective gloves if necessary.	No	Realized	Yes
<b>11.3</b>	<b>By people</b>					
<b>11.3.1</b>	<b>Misconduct in cooperation, self-assessment</b>					
	Avoid hazards and injuries.	Yes	Avoid working alone in the laboratory.	No	Realized	Yes

			Comment: Operating instructions, safety documentation			
<b>11.3.2</b>	<b>Misbehavior of guests and staff</b>					
	Avoid hazards and injuries.	Yes	Avoid solitary work Guests have to comply with the instructions of the operating staff or be in a secure area.	No	Realized	Yes
<b>11.4</b>	<b>By animals</b>					
<b>11.5</b>	<b>By plants and herbal products</b>					
<b>12</b>	<b>Psychological stress</b>					
<b>12.1</b>	<b>Work activity</b>					
<b>12.2</b>	<b>Work organization</b>					
<b>12.3</b>	<b>Social Conditions</b>					
<b>13</b>	<b>Organization</b>					
<b>13.1</b>	<b>Work routine</b>					
<b>13.2</b>	<b>Working hours</b>					
<b>13.3</b>	<b>Qualification</b>					
<b>13.3.1</b>	<b>Assignment for special activities</b>					
<b>13.4</b>	<b>Instruction</b>					
	Hazards of man and material due to improper work and non-compliance with regulations must be avoided.	Yes	Operating instructions, instruction (annual repetition), control.	No	Realized	Yes
<b>13.5</b>	<b>Responsibility</b>					
	Information	Yes	Proper safety information and working data is being provided.	No	Realized	Yes
<b>13.6</b>	<b>General organization</b>					

### 3.2 Implementation

Nr.	Possible hazards / loads	adequate measures	Measures (technical-organizational-personal) comments to implement measures	Consultancy requirements	Implementation Until/By	Effectiveness Effective/When
<b>1</b>	<b>Mechanical hazards</b>					
<b>1.1</b>	<b>Unprotected moving parts</b>					
<b>1.2</b>	<b>Parts with hazardous surfaces</b>					
	Sharpened/pointed electrodes tips	Yes	Assure tips are in the box. If they are changed during the experiment, handle them carefully.	No	Realized	Yes
<b>1.3</b>	<b>Moving means of transport, moving equipment</b>					
<b>1.4</b>	<b>Uncontrolled moving parts</b>					
<b>1.5</b>	<b>Fall on the plane, slipping, stumbling, kinking, failure (work and traffic areas)</b>					
<b>1.6</b>	<b>Fall</b>					
<b>2</b>	<b>Electrical hazards</b>					
<b>2.1</b>	<b>Dangerous body currents circulation</b>					
<b>2.2</b>	<b>Electric arcs</b>					
<b>3</b>	<b>Hazardous substances</b>					
<b>3.1</b>	<b>Gases</b>					
	N2, H2 and O2 production	Yes	N2 tank must be closed and all the valves related to N2 in the right position while performing the experiments.  H2 and O2 production must be controlled. Electrolysis is performed during a certain time. Follow instructions of H2 production document.	No	Realized	Yes
<b>3.2</b>	<b>Vapors</b>					
<b>3.3</b>	<b>Aerosols</b>					
<b>3.4</b>	<b>Liquids</b>					
	KOH solution	Yes	Solution recipient must be closed and correctly stored. Use gloves, glasses, overall and shoes.	No	Realized	Yes
<b>3.5</b>	<b>Solids</b>					

<b>3.6</b>	<b>Continuous reactions</b>					
<b>3.7</b>	<b>Dust</b>					
<b>4</b>	<b>Biological hazards</b>					
<b>4.1</b>	<b>Infection by microorganisms, viruses, or biological agents</b>					
<b>4.2</b>	<b>Genetically modified organisms (GMOs)</b>					
<b>4.3</b>	<b>Allergens and toxic substances of microorganisms, etc.</b>					
<b>5</b>	<b>Fire and explosions Risks</b>					
<b>5.1</b>	<b>Fire hazard due to solids, liquids, gases</b>					
	H2 combustion	Yes	Assure controlled H2 production. Follow instructions of H2 production document.	No	Realized	Yes
<b>5.2</b>	<b>Explosive atmosphere</b>					
<b>5.3</b>	<b>Explosives</b>					
<b>5.4</b>	<b>Electrostatic charge</b>					
<b>6</b>	<b>Thermal hazards</b>					
<b>6.1</b>	<b>Contact with hot media</b>					
<b>6.2</b>	<b>Contact with cold media</b>					
<b>7</b>	<b>Hazards due to special physical effects</b>					
<b>7.1</b>	<b>Noise</b>					
<b>7.2</b>	<b>Ultrasound, infrasound</b>					
<b>7.3</b>	<b>Whole body vibrations</b>					
<b>7.4</b>	<b>Hand-arm vibrations</b>					
<b>7.5</b>	<b>Non-ionizing radiation</b>					
	Laser	Yes	Follow the laser manual instructions.	No	Realized	Yes
<b>7.6</b>	<b>Ionizing radiation</b>					
<b>7.7</b>	<b>Electromagnetic fields</b>					
<b>7.8</b>	<b>Work in underpressure or overpressure</b>					

	Gas and liquid at high pressure	Yes	Check working pressure with pressure gauge. Physical protection has to be used (cover). Follow pressurization instructions and good practices.	No	Realized	Yes
<b>7.9</b>	<b>Danger of drowning</b>					
<b>8</b>	<b>Exposure to working environment</b>					
<b>8.1</b>	<b>Climate</b>					
<b>8.2</b>	<b>Lighting</b>					
<b>8.3</b>	<b>Space requirements / traffic routes</b>					
<b>9</b>	<b>Physical stress / workload</b>					
<b>9.1</b>	<b>Heavy dynamic work</b>					
<b>9.1.1</b>	<i>Lifting and carrying heavy loads</i>					
<b>9.2</b>	<b>One-sided dynamic work</b>					
<b>9.3</b>	<b>Posture / holding work</b>					
<b>9.4</b>	<b>Combination of static and dynamic work</b>					
<b>10</b>	<b>Perception and manageability</b>					
<b>10.1</b>	<b>Information photographing</b>					
<b>10.2</b>	<b>Scope of perception</b>					
<b>10.3</b>	<b>Difficult handling of work equipment</b>					
<b>11</b>	<b>Other hazards</b>					
<b>11.1</b>	<b>Unsuitable personal protective equipment</b>					
<b>11.2</b>	<b>Skin strain</b>					
	Contamination of hands during operation	Yes	Clean contaminated skin, skin protection plan is hanged. Wear gloves if necessary.	No	Realized	Yes
<b>11.3</b>	<b>By people</b>					
<b>11.3.1</b>	<b><i>Misconduct in cooperation, self-assessment</i></b>					
	Avoid hazards and injuries.	Yes	Avoid working alone in the laboratory. Comment: Operating instructions, safety documentation	No	Realized	Yes

<b>11.3.2</b>	<b>Misbehavior of guests and staff</b>					
	Avoid hazards and injuries.	Yes	Avoid solitary work Guests must comply with the instructions of the operating staff or be in a secure area, as is indicated in safety regulation.	No	Realized	Yes
<b>11.4</b>	<b>By animals</b>					
<b>11.5</b>	<b>By plants and herbal products</b>					
<b>12</b>	<b>Psychological stress</b>					
<b>12.1</b>	<b>Work activity</b>					
<b>12.2</b>	<b>Work organization</b>					
<b>12.3</b>	<b>Social Conditions</b>					
<b>13</b>	<b>Organization</b>					
<b>13.1</b>	<b>Work routine</b>					
<b>13.2</b>	<b>Working hours</b>					
<b>13.3</b>	<b>Qualification</b>					
<b>13.3.1</b>	<b>Assignment for special activities</b>					
<b>13.4</b>	<b>Instruction</b>					
	Hazards of man and material due to improper work and non-compliance with regulations must be avoided.	Yes	Operating instructions, instruction (annual repetition), control necessary	No	Realized	Yes
<b>13.5</b>	<b>Responsibility</b>					
	Information	Yes	Proper safety information and working data is being provided.	No	Realized	Yes
<b>13.6</b>	<b>Organization in general</b>					

### 3.3 Conclusion/Post-Procedure

Nr.					Implementation	Effectiveness
-----	--	--	--	--	----------------	---------------

	Possible hazards / loads	adequate measures	Measures (technical-organizational-personal) comments to implement measures	Consultancy requirements	Until/By	Effective/When
<b>1</b>	<b>Mechanical hazards</b>					
<b>1.1</b>	<b>Unprotected moving parts</b>					
<b>1.2</b>	<b>Parts with hazardous surfaces</b>					
	Sharpened/pointed electrodes tips	Yes	Store tips in correct box.	No	Realized	Yes
<b>1.3</b>	<b>Moving means of transport, moving equipment</b>					
<b>1.4</b>	<b>Uncontrolled moving parts</b>					
<b>1.5</b>	<b>Fall on the plane, slipping, stumbling, kinking, failure (work and traffic areas)</b>					
<b>1.6</b>	<b>Fall</b>					
<b>2</b>	<b>Electrical hazards</b>					
<b>2.1</b>	<b>Dangerous body currents circulation</b>					
<b>2.2</b>	<b>Electric arcs</b>					
<b>3</b>	<b>Hazardous substances</b>					
<b>3.1</b>	<b>Gases</b>					
	N2 H2 and O2 exhaust	Yes	Assure that N2 tank is closed and all the valves related to the gas circuit are in the right position. In case of N2 inhalation, follow N2 safety sheet instructions.  H2, O2 and N2 must be exhausted. Follow the exhaust procedure. If it is possible, do it near a window. Keep H2 and O2 out of flammability limits. Follow instructions of H2 production document.	No	Realized	Yes
<b>3.2</b>	<b>Vapors</b>					
<b>3.3</b>	<b>Aerosols</b>					
<b>3.4</b>	<b>Liquids</b>					
	KOH solution	Yes	Solution must be drained into the correct recipient for final storage.	No	Realized	Yes

			If solution is left in the electrolyzer make sure the electrodes or plugs are fixed. In order to avoid material damage, make sure KHO solution remains the permitted time inside the optical chamber.			
<b>3.5</b>	<b>Solids</b>					
<b>3.6</b>	<b>Continuous reactions</b>					
<b>3.7</b>	<b>Dust</b>					
<b>4</b>	<b>Biological hazards</b>					
<b>4.1</b>	<b>Infection by microorganisms, viruses, or biological agents</b>					
<b>4.2</b>	<b>Genetically modified organisms (GMOs)</b>					
<b>4.3</b>	<b>Allergens and toxic substances of microorganisms, etc.</b>					
<b>5</b>	<b>Fire and explosions Risks</b>					
<b>5.1</b>	<b>Fire hazard due to solids, liquids, gases</b>					
	H2 combustion	Yes	Assure controlled H2 exhaust. Follow instructions of H2 production document.	No	Realized	Yes
<b>5.2</b>	<b>Explosive atmosphere</b>					
<b>5.3</b>	<b>Explosives</b>					
<b>5.4</b>	<b>Electrostatic charge</b>					
<b>6</b>	<b>Thermal hazards</b>					
<b>6.1</b>	<b>Contact with hot media</b>					
<b>6.2</b>	<b>Contact with cold media</b>					
<b>7</b>	<b>Hazards due to special physical effects</b>					
<b>7.1</b>	<b>Noise</b>					
<b>7.2</b>	<b>Ultrasound, infrasound</b>					
<b>7.3</b>	<b>Whole body vibrations</b>					
<b>7.4</b>	<b>Hand-arm vibrations</b>					
<b>7.5</b>	<b>Non-ionizing radiation</b>					

	Laser	Yes	When turning it off, follow laser manual instructions.	No	Realized	Yes
<b>7.6</b>	<b>Ionizing radiation</b>					
<b>7.7</b>	<b>Electromagnetic fields</b>					
<b>7.8</b>	<b>Work in underpressure or overpressure</b>					
	Gas and liquid at high pressure	Yes	Follow depressurization instructions and good practices. The device must be depressurized, check pressure gauge.	No	Realized	Yes
<b>7.9</b>	<b>Danger of drowning</b>					
<b>8</b>	<b>Exposure to working environment</b>					
<b>8.1</b>	<b>Climate</b>					
<b>8.2</b>	<b>Lighting</b>					
<b>8.3</b>	<b>Space requirements / traffic routes</b>					
	Transporting and storing electrolyzer	Yes	If more experiments are going to be performed, do not modify space arrangement and experiment area. Make sure the electrolyzer is depressurized before transportation. Clear the path when moving the electrolyzer from one laboratory to another.	No	Realized	Yes
<b>9</b>	<b>Physical stress / workload</b>					
<b>9.1</b>	<b>Heavy dynamic work</b>					
<b>9.1.1</b>	<b>Lifting and carrying heavy loads</b>					
	Electrolyzer and needed equipment	Yes	Make sure to use the proper transportation means. Electrolyzer must be carried at least by two persons.	No	Realized	Yes
<b>9.2</b>	<b>One-sided dynamic work</b>					
<b>9.3</b>	<b>Posture / holding work</b>					
<b>9.4</b>	<b>Combination of static and dynamic work</b>					
<b>10</b>	<b>Perception and manageability</b>					
<b>10.1</b>	<b>Information photographing</b>					

<b>10.2</b>	<b>Scope of perception</b>					
<b>10.3</b>	<b>Difficult handling of work equipment</b>					
<b>11</b>	<b>Other hazards</b>					
<b>11.1</b>	<b>Unsuitable personal protective equipment</b>					
<b>11.2</b>	<b>Skin strain</b>					
	Contamination of hands during assembly work	Yes	Clean contaminated skin, skin protection plan is hanged. Wear protective gloves if necessary	No	Realized	Yes
<b>11.3</b>	<b>By people</b>					
<b>11.3.1</b>	<b><i>Misconduct in cooperation, self-assessment</i></b>					
	Avoid hazards and injuries.	Yes	Avoid working alone in the laboratory. Comment: Operating instructions, safety documentation	No	Realized	Yes
<b>11.3.2</b>	<b><i>Misbehavior of guests and staff</i></b>					
	Avoid hazards and injuries.	Yes	Avoid solitary work. Guests must comply with the instructions of the operating staff or be in a secure area, as is indicated in safety regulation.	No	Realized	Yes
<b>11.4</b>	<b>By animals</b>					
<b>11.5</b>	<b>By plants and herbal products</b>					
<b>12</b>	<b>Psychological stress</b>					
<b>12.1</b>	<b>Work activity</b>					
<b>12.2</b>	<b>Work organization</b>					
<b>12.3</b>	<b>Social Conditions</b>					
<b>13</b>	<b>Organization</b>					
<b>13.1</b>	<b>Work routine</b>					
<b>13.2</b>	<b>Working hours</b>					
<b>13.3</b>	<b>Qualification</b>					
<b>13.3.1</b>	<b><i>Assignment for special activities</i></b>					
<b>13.4</b>	<b>Instruction</b>					

	Hazards of man and material due to improper work and non-compliance with regulations must be avoided.	Yes	Operating instructions, instruction (annual repetition), control necessary	No	Realized	Yes
<b>13.5</b>	<b>Responsibility</b>					
	Information	Yes	Proper safety information and working data is being provided.	No	Realized	Yes
<b>13.6</b>	<b>Organization in general</b>					

### 3.4 Maintenance Service

Nr.	Possible hazards / loads	adequate measures	Measures (technical-organizational-personal) com- ments to implement measures	Consultancy requirements	implementation Until/By	effectiveness Effectiv/When
<b>1</b>	<b>Mechanical hazards</b>					
1.1	Unprotected moving parts					
1.2	Parts with hazardous surfaces					
1.3	Moving means of transport, moving equipment					
1.4	Uncontrolled moving parts					
1.5	Fall on the plane, slipping, stumbling, kinking, failure (work and traffic areas)					
1.6	Fall					
<b>2</b>	<b>Electrical hazards</b>					
2.1	Dangerous body currents circulation					
2.2	Electric arcs					
<b>3</b>	<b>Hazardous substances</b>					
3.1	Gases					

<b>3.2</b>	<b>Vapors</b>					
<b>3.3</b>	<b>Aerosols</b>					
<b>3.4</b>	<b>Liquids</b>					
	KOH solution	Yes	Clean the entire electrolyzer after removal of KOH solution. Use demineralized water for cleaning.	No	Realized	Yes
<b>3.5</b>	<b>Solids</b>					
<b>3.6</b>	<b>Continuous reactions</b>					
<b>3.7</b>	<b>Dust</b>					
<b>4</b>	<b>Biological hazards</b>					
<b>4.1</b>	<b>Infection by microorganisms, viruses, or biological agents</b>					
<b>4.2</b>	<b>Genetically modified organisms (GMOs)</b>					
<b>4.3</b>	<b>Allergens and toxic substances of microorganisms, etc.</b>					
<b>5</b>	<b>Fire and explosions Risks</b>					
<b>5.1</b>	<b>Fire hazard due to solids, liquids, gases</b>					
<b>5.2</b>	<b>Explosive atmosphere</b>					
<b>5.3</b>	<b>Explosives</b>					
<b>5.4</b>	<b>Electrostatic charge</b>					
<b>6</b>	<b>Thermal hazards</b>					
<b>6.1</b>	<b>Contact with hot media</b>					
<b>6.2</b>	<b>Contact with cold media</b>					
<b>7</b>	<b>Hazards due to special physical effects</b>					
<b>7.1</b>	<b>Noise</b>					
<b>7.2</b>	<b>Ultrasound, infrasound</b>					
<b>7.3</b>	<b>Whole body vibrations</b>					
<b>7.4</b>	<b>Hand-arm vibrations</b>					
<b>7.5</b>	<b>Non-ionizing radiation</b>					

<b>7.6</b>	<b>Ionizing radiation</b>					
<b>7.7</b>	<b>Electromagnetic fields</b>					
<b>7.8</b>	<b>Work in underpressure or overpressure</b>					
	Gas and liquid at high pressure	Yes	Look for damaged parts (connections, tubs). Check proper functioning of pressure gauge.	No	Realized	Yes
<b>7.9</b>	<b>Danger of drowning</b>					
<b>8</b>	<b>Exposure to working environment</b>					
<b>8.1</b>	<b>Climate</b>					
<b>8.2</b>	<b>Lighting</b>					
<b>8.3</b>	<b>Space requirements / traffic routes</b>					
	Transporting and installation of electrolyzer	Yes	Make sure is enough space to mount all the needed equipment.	No	Realized	Yes
<b>9</b>	<b>Physical stress / workload</b>					
<b>9.1</b>	<b>Heavy dynamic work</b>					
<b>9.1.1</b>	<b><i>Lifting and carrying heavy loads</i></b>					
<b>9.2</b>	<b>One-sided dynamic work</b>					
<b>9.3</b>	<b>Posture / holding work</b>					
<b>9.4</b>	<b>Combination of static and dynamic work</b>					
<b>10</b>	<b>Perception and manageability</b>					
<b>10.1</b>	<b>Information photographing</b>					
<b>10.2</b>	<b>Scope of perception</b>					
<b>10.3</b>	<b>Difficult handling of work equipment</b>					
<b>11</b>	<b>Other hazards</b>					
<b>11.1</b>	<b>Unsuitable personal protective equipment</b>					
<b>11.2</b>	<b>Skin strain</b>					
<b>11.3</b>	<b>By people</b>					

<b>11.3.1</b>	<b>Misconduct in cooperation, self-assessment</b>					
<b>11.3.2</b>	<b>Misbehavior of guests and staff</b>					
<b>11.4</b>	<b>By animals</b>					
<b>11.5</b>	<b>By plants and herbal products</b>					
<b>12</b>	<b>Psychological stress</b>					
<b>12.1</b>	<b>Work activity</b>					
<b>12.2</b>	<b>Work organization</b>					
<b>12.3</b>	<b>Social Conditions</b>					
<b>13</b>	<b>Organization</b>					
<b>13.1</b>	<b>Work routine</b>					
<b>13.2</b>	<b>Working hours</b>					
<b>13.3</b>	<b>Qualification</b>					
<b>13.3.1</b>	<b>Assignment for special activities</b>					
	Maintenance	Yes	The operator must prove the appropriate qualification. (Pressure test) Comment: Operating instructions, instruction, control necessary.	No	Realized	Yes
<b>13.4</b>	<b>Instruction</b>					
	Hazards of man and material due to improper work and non-compliance with regulations must be avoided.	Yes	Operating instructions, instruction (annual repetition), control necessary	No	Realized	Yes
<b>13.5</b>	<b>Responsibility</b>					
	Information	Yes	Proper safety information and working data is being provided.	No	Realized	Yes
<b>13.6</b>	<b>Organization in general</b>					

## **4 Special safety rules**

Checklist, escape routes, responsibility list, instructions

## **5 Exposure Areas**

## **6 Instruction for guests**

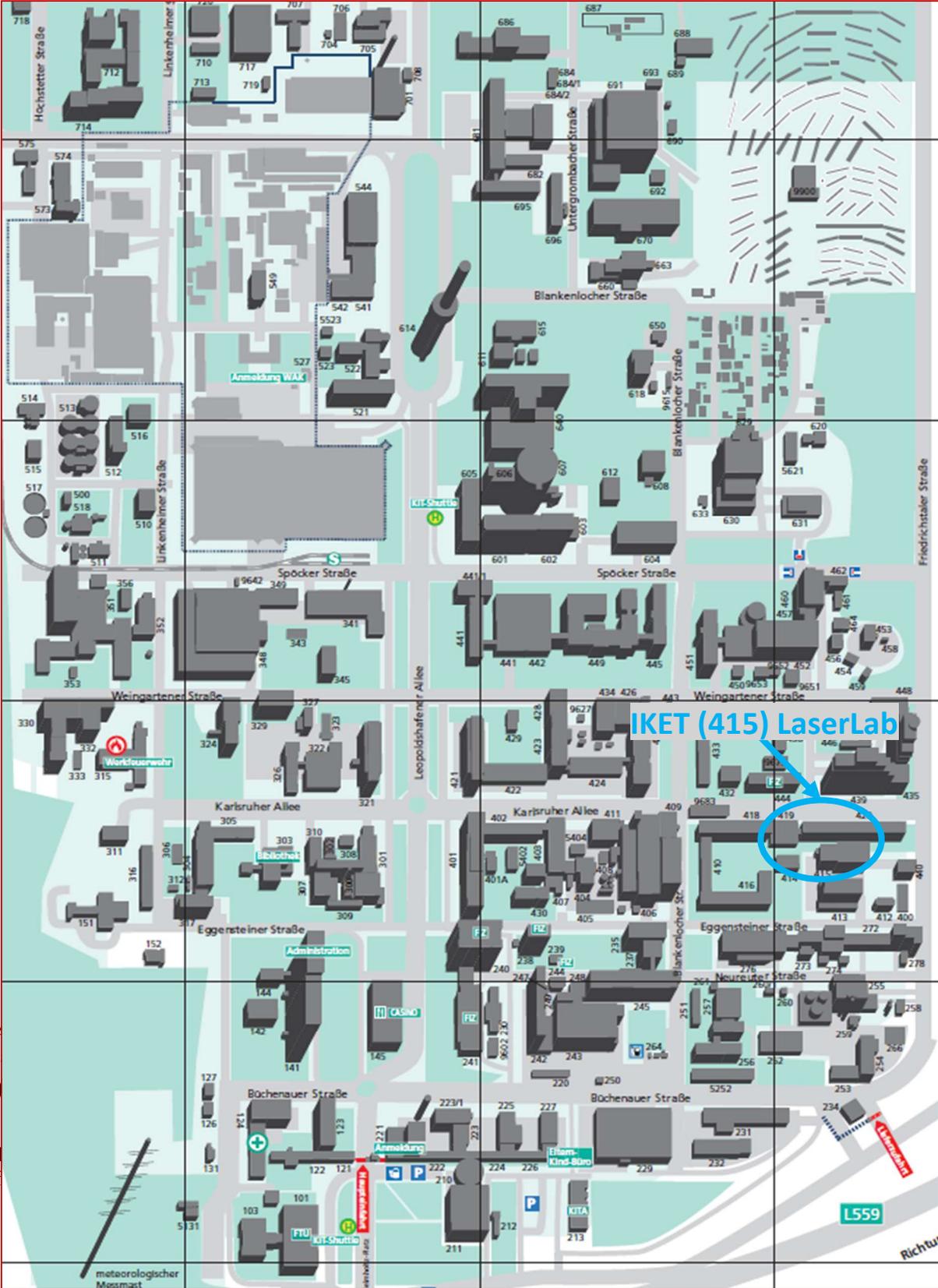
Before starting the experiment, a safety instruction is required. The protocol to be used is in the appendix.

# **Appendix A**

For hazard assessment High Pressure Electrolyzer



# A-1 Site plan containing laser laboratory with HPE



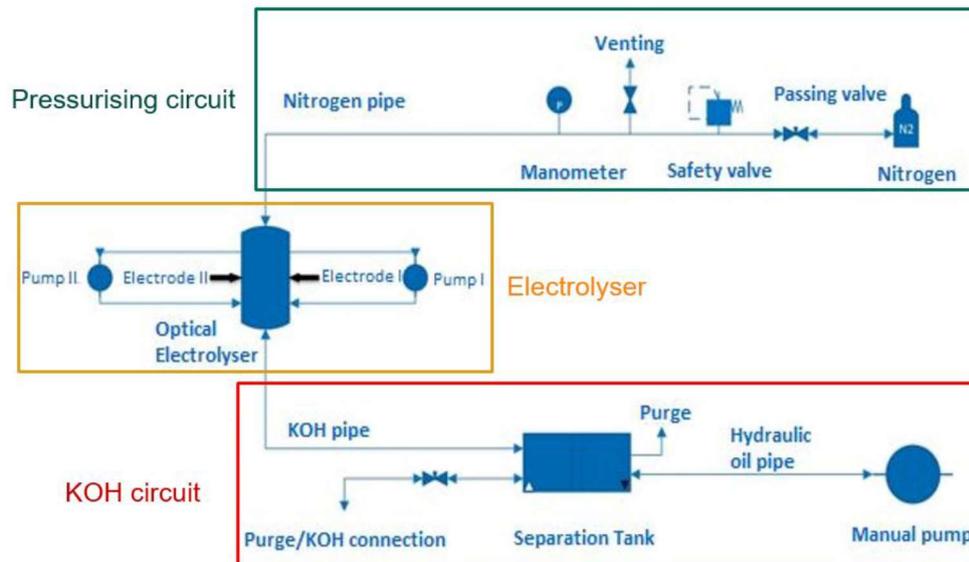


Fig.2 A-2: High pressure electrolyzer.

The optical electrolyzer consists of a cylinder with eight connections. Two connections are for the electrodes, two more to fill and exhaust/drain the chamber with nitrogen/electrolyte correspondingly and the last four are for the recirculation pumps. There are also two glass windows, which make it possible to take optical measurements of the hydrogen bubbles produced during electrolysis.

The electrolyzer chamber is designed to resist a working pressure of up to 450bar. The device has two configurations. With the first one, pressures can be rise only up to 200bar. The second configuration is able to withstand pressures of up to 450bar.

Electrodes are exchangeable, in order to have different types of electrode shapes and sizes.

Nitrogen is contained in a high-pressure bottle and fed in through the passing valve, which is linked to the main cylinder of the optical electrolyzer. A pressure gauge measures the total pressure on the system and the safety valve ensures the pressure does not exceed the limit (210bar conf.1/450bar conf.2).

The hydraulic tank and the manual pump are connected to the system. This tank leads to two separated circuits. The first one is connected to the main tank, filled with the electrolyte. The second circuit is filled with hydraulic oil and connected to the manual pump. A piston inside this tank separates both liquids. The manual pump is used to raise the pressure above 200bar. The pump is connected to the hydraulic oil circuit.

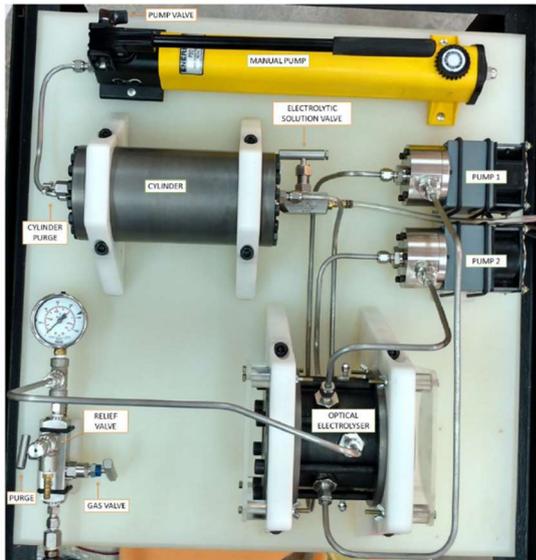


Fig.1 A-2: High pressure electrolyzer.

In Fig. 3 shows the arrangement used to perform the experiments.

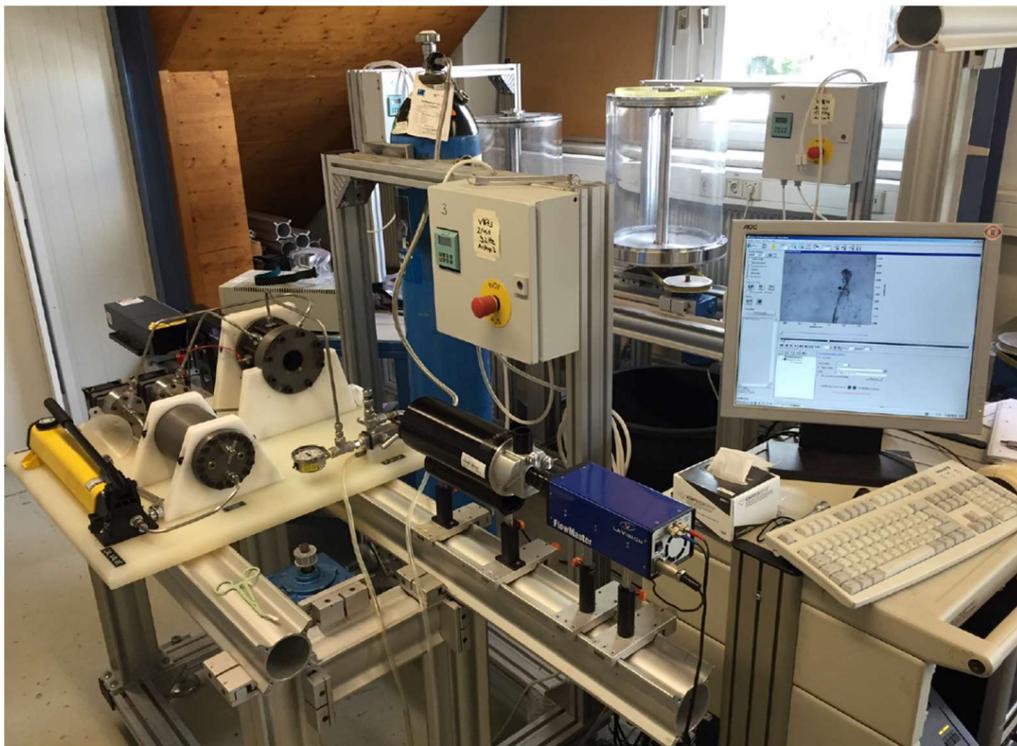


Fig.3 A-2: Experimental arrangement.

As it can be seen, more equipment is needed, this is mentioned in section C-1

## A-3 List of first aids responsible.

T Table A-1: First Aids responsables at the IKET and in the B 415 Laser Lab,

Name	Telenor.
Albrecht	24485
Abrogate	23463/24097
<b>Bauru</b>	<b>22174/26203</b>
Croon	23818
Dauber	23461
Hesselschwerdt, M.	26204
Kaup	24810
Kirstahler	23351/23355
Krieger	23485
Landmann	23785
Meyer, M.	26204
Miodek,	23485
<u>Pflaum</u>	<u>28266</u>
Prestel	24070
Rapp	24887/24017
Rottenecker	23480
Schmidt-Stiefel	23453
<u>Sempert</u>	<u>28266</u>
Schwall	26592/23352
Vollmer	23460
Wenz	26205
Wiegner	22416
Wiemer	23472

NOTRUF: 3333

## A-4 Protocol on the instruction for guest scientists and third-party personnel

 Karlsruher Institut für Technologie
<b>Protokoll über die Einweisung von Fremdfirmenpersonal</b>
<b>NOTRUF: 3333</b>
Firma/Firmenanschrift _____
Die/Der Eingewiesene: _____ (Name)
Abruf-/Auftrags-/Pos-Nr. _____
Einsatzort _____ (Institut, Bau, Raum, Anlage)
Durchzuführende Arbeiten _____ _____ (Leistungsbeschreibung - Kurztext)
<b>1. Allgemeine Einweisungsthemen (hier sind konkrete Angaben und genaue Bezeichnungen der aufgeführten Punkte erforderlich):</b>
<input type="checkbox"/> Baustellenordnung des KIT - Campus Nord
<input type="checkbox"/> Allgemeine Sicherheitsregelung des KIT - Campus Nord
<input type="checkbox"/> Sonstige Rechtsvorschriften, behördliche Genehmigungen und Auflagen, interne Regelungen _____ _____
<input type="checkbox"/> Spezielle Sicherheitsanweisungen im Arbeits- und Umweltschutz: _____ _____
<input type="checkbox"/> Zusätzliche Einweisungsthemen: _____ _____

**2. Besondere Einweisungsthemen (hier sind konkrete Angaben und genaue Bezeichnungen der aufgeführten Punkte notwendig):**

Fluchtwege/Fluchtplan

Brandschutz/besondere Brandschutzvorschriften

Konkrete Gefahren am Einsatzort

Besondere betriebliche Abläufe des Institutes/der Abteilung:

Gefahren durch Gefahrstoffe (z.B. krebserzeugende Stoffe)

Strahlenschutzbelehrung wird durch Strahlenschutzbeauftragten durchgeführt (Protokoll liegt bei)

Mögliche Auswirkungen der durchzuführenden Arbeiten auf den lfd. Betrieb der Abteilung/des Institutes, in der/dem die Arbeiten ausgeführt werden

Tätigkeit anderer Fremdfirmen/Personal des AG im Arbeitsbereich des Auftragnehmers:

(kurze Beschreibung der Tätigkeit und der gegenseitigen Gefährdung)

Sicherheitskoordinator gemäß § 6 BGV A 1 erforderlich:

Name: \_\_\_\_\_ Institut: \_\_\_\_\_ Tel.: \_\_\_\_\_

Übergebene Unterlagen:

Baustellenordnung des KIT - Campus Nord

Allgemeine Sicherheitsregelung des KIT - Campus Nord

Im Rahmen des Auftrags bereits erhaltene Unterlagen:

Ich bestätige durch meine Unterschrift, dass ich vor der Arbeitsaufnahme mit den örtlichen Gegebenheiten vertraut gemacht wurde sowie auf Besonderheiten und Gefahren, die mit der Tätigkeit verbunden sind, hingewiesen wurde.

Ich bestätige auch, dass ich in die gekennzeichneten Themen eingewiesen, insbesondere in die für den Arbeits- und Umweltschutz im KIT geltenden Rechtsvorschriften, behördlichen Maßnahmen, internen Regelungen, Sicherheitsanweisungen, Unfallverhütungsvorschriften (UVV), deren Einhaltung ich bei der Auftragsdurchführung sicherstellen werde.

Die aufgeführten Unterlagen habe ich erhalten.

Den Inhalt der Einweisung habe ich verstanden.

\_\_\_\_\_  
(Ort und Datum)

\_\_\_\_\_  
(Name der/des Eingewiesenen)

\_\_\_\_\_  
(Unterschrift der/des Eingewiesenen)

\_\_\_\_\_  
(Name der/des Eingewiesenen)

\_\_\_\_\_  
(Unterschrift der/des Eingewiesenen)

\_\_\_\_\_  
(Name der/des Eingewiesenen)

\_\_\_\_\_  
(Unterschrift der/des Eingewiesenen)

**Einweisung durchgeführt:**

\_\_\_\_\_  
(Ort und Datum)

\_\_\_\_\_  
(Name Einweisender, Ziffer 1)

\_\_\_\_\_  
(Unterschrift Einweisender, Ziffer 1)

\_\_\_\_\_  
(Name Einweisender, Ziffer 2)

\_\_\_\_\_  
(Unterschrift Einweisender, Ziffer 2)

## A-5 Checklist for the experiments

For the planned experiments in the HPE, checklists are provided. After checking the experimental facilities, the list can then be adapted to the respective requirements and extended if necessary. The examiner fills the checklists and provides them with the signature, date and test number.

<input type="checkbox"/>	All the needed equipment is already placed and arranged properly.
<input type="checkbox"/>	Safety measurements: Cloth, Electrolyzer in container and covered up, exhaust container placed.
<input type="checkbox"/>	All valves are closed and power sources is turned off.
<input type="checkbox"/>	The electrolyzer is empty and the electrodes are fixed.
<input type="checkbox"/>	Check for any damaged parts.
<input type="checkbox"/>	Open passive valve and KOH valve.
<input type="checkbox"/>	Fill chamber with N <sub>2</sub> until there is no remaining air.
<input type="checkbox"/>	Close KOH valve.
<input type="checkbox"/>	Close N <sub>2</sub> valve and pasive valve.
<input type="checkbox"/>	Fill the plastic tube with KOH and open the KOH valve. Use KOH until there is the right amount in the optical chamber.
<input type="checkbox"/>	To rise the pressure to the working value open N <sub>2</sub> tank and passive valve again. Close them when the desire pressure is reached. Check with pressure gauge.
<input type="checkbox"/>	Turn on the measurement and data equipment. Laser, camera and computer.
<input type="checkbox"/>	Check measurement equipment and data acquisition is functioning properly.
<input type="checkbox"/>	Connect the electrodes to the power supply.
<input type="checkbox"/>	Turn on the power supply.
<input type="checkbox"/>	Acquire optical measurements.
<input type="checkbox"/>	When finishing the measurements, turn off the power supply.
<input type="checkbox"/>	Save data measurements.
<input type="checkbox"/>	Turn off optical equipment.
<input type="checkbox"/>	Disconnect electrodes.
<input type="checkbox"/>	Exhaust gases by opening the exhaust valve, until atmospheric pressure is reached. Close valves.
<input type="checkbox"/>	Open KOH valve, drain KOH solution. Ocular inspection.
<input type="checkbox"/>	Change electrodes and repeat all steps.

## A-6 List of responsibilities

The employees involved in the HPE experiments and their responsibilities are summarized in Table A2. These persons are authorized to participate in the construction, implementation and monitoring of the tests. By signing it, they confirm that they have read and understood the present working and safety instructions and will follow the work to be carried out.

*Table A-2: Personnel and responsibility list*

Name (Tel.)	Organization	Tasks	Date, Signature
T. Jordan (26105)	IKET	Administrative Gesamtkoordination, Arbeitsschutz und Sicherheit	
M. Kuznetsov (24716)	IIET	Wissenschaftliche Planung, Testmatrix, Verantwortlicher Versuchsleiter für Vorbereitung und Durchführung, Checklisten	
J. Prieb-Brunner (23835)	StFA	Arbeitssicherheit	



## **Appendix B**

For hazard assessment of high pressure electrolyzer



# B-1 Nitrogen Safety Data Sheet

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 1 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

## ABSCHNITT 1. Bezeichnung des Stoffs bzw. des Gemischs und Firmenbezeichnung

### 1.1. Produktidentifikator

Handelsname	: Stickstoff (verdichtet) , Stickstoff (N40, N50, N50 COfrei, N50 ECD, N60), N2 IMPLANT N50, N2 PURGE N60
Sicherheitsdatenblatt-Nr.	: 089A
Chemische Bezeichnung	: Stickstoff CAS-Nr. : 7727-37-9 EG-Nr. : 231-783-9 Index-Nr. : --
Registrierungs-Nr.	: Aufgeführt in Anhang IV / V REACH, von der Registrierung ausgenommen.
Chemische Formel	: N2

### 1.2. Relevante identifizierte Verwendungen des Stoffs oder Gemischs und Verwendungen, von denen abgeraten wird

**Relevante identifizierte Verwendungen :** Industriell und berufsmäßig. Vor Anwendung Gefährdungsbeurteilung durchführen. Prüfgas / Kalibriergas. Laborzwecke. Spülgas, Verdünnungsgas, Inertisierungsgas. Schutzgas für Schweißprozesse. Zur Herstellung von Komponenten in der Elektronik- / Photovoltaikindustrie.  
Kontaktieren Sie Ihren Lieferanten für weitere Informationen über Verwendungen.

### 1.3. Einzelheiten zum Lieferanten, der das Sicherheitsdatenblatt bereitstellt

Bezeichnung des Unternehmens	: AIR LIQUIDE Deutschland GmbH Hans-Günther-Sohl-Straße 5 D-40235 Düsseldorf GERMANY Telefon: +49 (0)211 6699-0 - Fax: +49 (0)211 6699-222
E-Mail-Adresse (der sachkundigen Person)	: Info.SDB@AirLiquide.de

### 1.4. Notrufnummer

Notfall-Telefonnummer	: +49 (0)2151 398668
- Verfügbarkeit	: ( 24 / 7 )

## ABSCHNITT 2. Mögliche Gefahren

### 2.1. Einstufung des Stoffs oder Gemischs

#### Gefahrenklasse, Gefahrenkategorie und Gefahrenkodierung, Verordnung (EG) Nr. 1272/2008 (CLP)

• **Physikalische Gefahren** : Unter Druck stehende Gase - verdichtete Gase - Achtung - (CLP : Press. Gas) - H280

#### Einstufung nach EG 67/548 oder EG 1999/45.

**Einstufung** : In Anhang VI CLP nicht genannt.  
Keine EG Kennzeichnung erforderlich.  
Nicht als gefährlicher Stoff / gefährliches Gemisch eingestuft.

### 2.2. Kennzeichnungselemente

#### Kennzeichnung nach Verordnung EG 1272/2008 (CLP).

• Gefahren Piktogramm(e)



• **Gefahrenpiktogramm Code** : GHS04  
• **Signalwort** : Achtung

AIR LIQUIDE Deutschland GmbH  
Hans-Günther-Sohl-Straße 5 D-40235 Düsseldorf GERMANY  
Telefon: +49 (0)211 6699-0 - Fax: +49 (0)211 6699-222

Im Notfall : +49 (0)2151 398668

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 2 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

## ABSCHNITT 2. Mögliche Gefahren (Forts.)

- Gefahrenhinweise : H280 - Enthält Gas unter Druck; kann bei Erwärmung explodieren.
- Sicherheitshinweise
- Lagerung : P403 - An einem gut belüfteten Ort aufbewahren.

### 2.3. Sonstige Gefahren

- Sonstige Gefahren : Erstickend in hohen Konzentrationen.

## ABSCHNITT 3. Zusammensetzung/Angaben zu Bestandteilen

### 3.1. Stoff / 3.2. Gemisch

Stoff.

Stoffbezeichnung	Inhalt [Vol-%]	CAS-Nr. EG-Nr. Index-Nr. Registrierungs-Nr.	Einstufung(DSD)	Einstufung(CLP)
Stickstoff	:	100 %	7727-37-9 231-783-9 ---	Not classified (DSD/DPD) Press. Gas (H280)

Enthält keine anderen Komponenten oder Verunreinigungen, die die Einstufung dieses Produktes beeinflussen.

- \* 1: Aufgeführt in Anhang IV / V REACH, von der Registrierung ausgenommen.
  - \* 2: Registrierungszeitraum noch nicht abgelaufen.
  - \* 3: Registrierung nach REACH nicht erforderlich: Stoff wird importiert < 1t/a.
- Volltext der R-Sätze siehe Abschnitt 16. Volltext der Gefahrenhinweise siehe Abschnitt 16.

## ABSCHNITT 4. Erste-Hilfe-Maßnahmen

### 4.1. Beschreibung der Erste-Hilfe-Maßnahmen

- Einatmen : Das Opfer ist unter Benutzung eines umluftunabhängigen Atemgerätes in frische Luft zu bringen. Warm und ruhig halten. Arzt hinzuziehen. Bei Atemstillstand künstliche Beatmung.
- Hautkontakt : Schädliche Wirkungen dieses Produktes werden nicht erwartet.
- Augenkontakt : Schädliche Wirkungen dieses Produktes werden nicht erwartet.
- Verschlucken : Verschlucken wird nicht als möglicher Weg der Exposition angesehen.

### 4.2. Wichtigste akute und verzögert auftretende Symptome und Wirkungen

- : Hohe Konzentrationen können Ersticken verursachen. Symptome können Verlust der Bewegungsfähigkeit und des Bewusstseins sein. Das Opfer bemerkt das Ersticken nicht.

### 4.3. Hinweise auf ärztliche Soforthilfe oder Spezialbehandlung

- : Keine.

	<b>SICHERHEITSDATENBLATT</b> gemäß RL 1907/2006/EG (REACH)	Seite : 3 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

#### ABSCHNITT 5. Maßnahmen zur Brandbekämpfung

##### 5.1. Löschmittel

- Geeignete Löschmittel : Wassersprühstrahl oder Wassemebel.
- Ungeeignete Löschmittel : Wasserstrahl zum Löschen ungeeignet.

##### 5.2. Besondere vom Stoff oder Gemisch ausgehende Gefahren

- Spezielle Risiken : Einwirkung von Feuer kann Bersten / Explodieren des Behälters verursachen.
- Gefährliche Verbrennungsprodukte : Keine.

##### 5.3. Hinweise für die Brandbekämpfung

- Spezifische Methoden : Behälter aus dem Wirkungsbereich des Brandes entfernen, wenn dies gefahrlos möglich ist. Wenn möglich, Gasaustritt stoppen. Maßnahmen der Brandbekämpfung auf den Brand in der Umgebung abstimmen. Druckbehälter können bersten, wenn sie direktem Feuer bzw. Wärmestrahlung durch Feuer ausgesetzt sind. Gefährdete Druckbehälter mit Wassersprühstrahl aus geschützter Position kühlen. Schadstoffbelastetes Löschwasser nicht in Abflüsse und die Kanalisation gelangen lassen. Wassersprühstrahl oder Wassemebel einsetzen, um Rauch niederzuschlagen.
- Spezielle Schutzausrüstung für die Feuerwehr : Umluftunabhängiges Atemgerät benutzen. Standard EN 137 - Umluftunabhängige Atemschutzgeräte mit Vollgesichtsmaske. Standardschutzkleidung und -ausrüstung (Umluftunabhängiges Atemschutzgerät) für die Feuerwehr. Standard EN 469 - Schutzkleidung für die Feuerwehr. Standard EN 659 - Schutzhandschuhe für die Feuerwehr.

#### ABSCHNITT 6. Maßnahmen bei unbeabsichtigter Freisetzung

##### 6.1. Personenbezogene Vorsichtsmaßnahmen, Schutzausrüstungen und in Notfällen anzuwendende Verfahren

- : Beim Betreten des Bereiches umluftunabhängiges Atemgerät benutzen, sofern nicht die Ungefährlichkeit der Atmosphäre nachgewiesen ist. Für ausreichende Lüftung sorgen. Gebiet räumen. Versuchen, den Gasaustritt zu stoppen. Örtlichen Alarmplan beachten. Auf windzugewandter Seite bleiben.

##### 6.2. Umweltschutzmaßnahmen

- : Versuchen, den Gasaustritt zu stoppen.

##### 6.3. Methoden und Material für Rückhaltung und Reinigung

- : Umgebung belüften.

##### 6.4. Verweis auf andere Abschnitte

- Verweis auf andere Abschnitte : Siehe auch Abschnitte 8 und 13.

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 4 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

## ABSCHNITT 7. Handhabung und Lagerung

### 7.1. Schutzmaßnahmen zur sicheren Handhabung

- |  |   |
|--|---|
| Sicherer Umgang mit dem Stoff            | : Nur solche Ausrüstung verwenden, die für dieses Produkt und den vorgesehenen Druck und Temperatur geeignet ist. Im Zweifelsfall den Gaslieferanten konsultieren.<br>Beim Umgang mit dem Produkt nicht rauchen.<br>Nur erfahrene und entsprechend geschulte Personen sollten unter Druck befindliche Gase handhaben.<br>Stellen Sie sicher, dass das gesamte Gassystem vor dem Gebrauch (und danach regelmäßig) auf Lecks geprüft wurde (wird).<br>Umgang mit dem Produkt im Einklang mit allgemeinen Arbeitsschutzmaßnahmen und Sicherheitsanweisungen.<br>Sicherheitsventil(e) in Gasanlagen vorsehen.<br>Produktaustritt an die Atmosphäre vermeiden.<br>Gas nicht einatmen.  |
| Sicherer Umgang mit dem Druckgasbehälter | : Eindringen von Wasser in den Gasbehälter verhindern.<br>Bedienungshinweise des Gaslieferanten beachten.<br>Rückströmung in den Gasbehälter verhindern.<br>Setzen Sie die Auslasskappen oder -stöpsel und die Ventilschutzkappe wieder auf, sobald der Behälter von der Anlage getrennt wird.<br>Gasflaschen vor mechanischer Beschädigung schützen; nicht ziehen, nicht rollen, nicht schieben, nicht fallen lassen.<br>Das Produktetikett dient der Identifizierung des Inhalts der Gasflasche und darf nicht entfernt oder unkenntlich gemacht werden.<br>Für den Transport von Gasflaschen, selbst auf kurzen Strecken, immer einen Flaschenwagen oder anderen geeigneten Handwagen benutzen.<br>Ventilschutzkappe nicht entfernen bevor die Flasche an einer Wand oder einen Labortisch oder auf einen Flaschenständer gestellt wurde, und zum Gebrauch bereit ist.<br>Falls der Benutzer irgendwelche Schwierigkeiten bei der Bedienung des Flaschenventils bemerkt, den Gebrauch unterbrechen und Kontakt mit dem Lieferanten aufnehmen.<br>Das Ventil des Behälters nach jedem Gebrauch und nach der Entleerung schließen, auch wenn er noch immer angeschlossen ist.<br>Versuchen Sie nie, Ventile oder Sicherheitsdruckentlastungseinrichtungen am Behälter zu reparieren.<br>Ventilanschlüsse des Behälters sauber und frei von Verunreinigungen halten, insbesondere frei von Öl und Wasser.<br>Versuchen Sie nicht, das Gas von einer Gasflasche oder Behälter in einen anderen umzufüllen.<br>Benutzen Sie nie Flammen oder elektrische Heizgeräte zur Druckerhöhung im Behälter.<br>Beschädigungen an diesen Einrichtungen müssen umgehend dem Lieferanten mitgeteilt werden. |

### 7.2. Bedingungen zur sicheren Lagerung unter Berücksichtigung von Unverträglichkeiten

- : Behälter bei weniger als 50°C an einem gut gelüfteten Ort lagern. Die Behälter sollten an einem Ort ohne Brandgefahr und entfernt von Wärme- und Zündquellen gelagert werden. Gelagerte Flaschen sollten regelmäßig auf Leckagen und korrekte Lagerbedingungen geprüft werden.
- Alle Vorschriften und örtlichen Erfordernisse an die Lagerung von Behältern müssen eingehalten werden.
- Die Behälter nicht unter Bedingungen lagern, die die Korrosion beschleunigen. Behälter aufrecht stehend lagern und gegen Umfallen sichern. Ein Ventilschutzring sollte vorhanden sein oder die Ventilschutzkappe angebracht werden. Von brennbaren Stoffen fernhalten.

### 7.3. Spezifische Endanwendungen

- : Keine.

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 5 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

#### ABSCHNITT 8. Begrenzung und Überwachung der Exposition/Persönliche Schutzausrüstungen

##### 8.1. Zu überwachende Parameter

DNEL: Abgeleiteter Nicht Effekt Level (Beschäftigte)

: Es liegen keine Angaben vor.

PNEC: Predicted no effect concentration

: Es liegen keine Angaben vor.

##### 8.2. Begrenzung und Überwachung der Exposition

- 8.2.1. Geeignete technische Steuerungseinrichtungen** : Allgemeine und lokale Absaugung vorsehen. Anlagen, die unter Druck stehen, sollten regelmäßig auf Dichtheit geprüft werden. Sauerstoff-Detektoren einsetzen, falls erstickend wirkende Gase emittiert werden können. Arbeitserlaubnisverfahren z.B. bei Wartungsarbeiten in Betracht ziehen.
- 8.2.2. Individuelle Schutzmaßnahmen, z.B. Persönliche Schutzausrüstung** : Eine Gefährdungsbeurteilung sollte für alle Arbeitsbereiche erstellt und dokumentiert sein, in der alle Risiken der Verwendung des Produktes erfasst sind und die erforderliche persönliche Schutzausrüstung abgeleitet wird. Die folgenden Empfehlungen sollten in Betracht gezogen werden:  
 Persönliche Schutzausrüstung, die in Übereinstimmung mit EN / ISO-Normen steht, auswählen.
- **Augen- / Gesichtsschutz** : Schutzbrille mit Seitenschutz tragen. Standard EN 166 - Persönlicher Augenschutz.
  - **Hautschutz**
    - **Handschutz** : Bei der Handhabung von Druckbehältern / Druckgasflaschen Arbeitshandschuhe tragen. Standard EN 388 - Schutzhandschuhe gegen mechanische Risiken.
    - **Sonstige Schutzmaßnahmen** : Beim Umgang mit Druckgasflaschen / Druckbehältern Sicherheitsschuhe tragen. Standard EN ISO 20345 - Persönliche Schutzausrüstung - Sicherheitsschuhe.
  - **Atemschutz** : Umluftunabhängiges Atemschutzgerät oder eine Druckluftleitung mit Maske in im Fall von sauerstoffreduzierter Atmosphäre verwenden. Standard EN 137 - Umluftunabhängige Atemschutzgeräte mit Vollgesichtsmaske.
  - **Thermische Gefahren** : Keine erforderlich.
- 8.2.3. Begrenzung und Überwachung der Umweltexposition** : Keine erforderlich.

#### ABSCHNITT 9. Physikalische und chemische Eigenschaften

##### 9.1. Angaben zu den grundlegenden physikalischen und chemischen Eigenschaften

- Aussehen**
- Physikalischer Zustand bei 20°C / 101.3kPa : Gas.
- Farbe : Farblos.
- Geruch : Keine Warnung durch Geruch.
- Geruchsschwelle : Geruchswahrnehmung ist subjektiv und nicht geeignet, um vor einer Überexposition zu warnen.
- pH-Wert : Nicht anwendbar.
- Molmasse [g/mol] : 28
- Schmelzpunkt [°C] : -210
- Siedepunkt [°C] : -196
- Kritische Temperatur [°C] : -147
- Flammpunkt [°C] : Nicht anwendbar auf Gase und Gasgemische

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 6 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

#### ABSCHNITT 9. Physikalische und chemische Eigenschaften (Forts.)

Verdampfungsgeschwindigkeit (Äther=1)	: Nicht anwendbar auf Gase und Gasgemische
Zündgrenzen [Vol.% in Luft]	: Nicht brennbar.
Dampfdruck [20°C]	: Nicht anwendbar.
Relative Dichte, Gas (Luft=1)	: 0,97
Relative Dichte, flüssig (Wasser=1)	: Nicht anwendbar.
Löslichkeit in Wasser [mg/l]	: 20
Verteilungskoeffizient n-Oktanol/Wasser [log Kow]	: Nicht anwendbar auf anorganische Gase
Zündtemperatur [°C]	: Nicht anwendbar.
Viskosität bei 20°C [mPa.s]	: Nicht anwendbar.
Explosive Eigenschaften	: Nicht anwendbar.
Oxidierende Eigenschaften	: Keine.

#### 9.2. Sonstige Angaben

Sonstige Angaben	: Keine.
------------------	----------

#### ABSCHNITT 10. Stabilität und Reaktivität

#### 10.1. Reaktivität

: Keine Gefahren durch Reaktivität außer denen, die in den nachfolgenden Unterabschnitten beschrieben sind.

#### 10.2. Chemische Stabilität

: Stabil unter normalen Bedingungen.

#### 10.3. Möglichkeit gefährlicher Reaktionen

: Keine.

#### 10.4. Zu vermeidende Bedingungen

: Keine unter den empfohlenen Bedingungen bei Verwendung und Lagerung (Siehe Abschnitt 7).

#### 10.5. Unverträgliche Materialien

: Keine.  
Weitere Informationen zur Materialverträglichkeit: siehe ISO11114.

#### 10.6. Gefährliche Zersetzungsprodukte

: Keine.

#### ABSCHNITT 11. Toxikologische Angaben

#### 11.1. Angaben zu toxikologischen Wirkungen

Akute Toxizität	: Toxische Wirkungen des Produkts sind nicht bekannt.
Ätz-/Reizwirkung auf die Haut	: Keine Wirkungen des Produktes bekannt.
schwere Augenschädigung/-reizung	: Keine Wirkungen des Produktes bekannt.
Sensibilisierung der Atemwege/Haut	: Keine Wirkungen des Produktes bekannt.
Kanzerogenität	: Keine Wirkungen des Produktes bekannt.
Mutagenität	: Keine Wirkungen des Produktes bekannt.

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 7 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

#### ABSCHNITT 11. Toxikologische Angaben (Forts.)

Reproduktionstoxizität	: Keine Wirkungen des Produktes bekannt.
Spezifische Zielorgan-Toxizität bei einmaliger Exposition	: Keine Wirkungen des Produktes bekannt.
Spezifische Zielorgan-Toxizität bei wiederholter Exposition	: Keine Wirkungen des Produktes bekannt.
Aspirationsgefahr	: Nicht anwendbar auf Gase und Gasgemische

#### ABSCHNITT 12. Umweltbezogene Angaben

##### 12.1. Toxizität

Bewertung : Das Produkt verursacht keine Umweltschäden.

##### 12.2. Persistenz und Abbaubarkeit

Bewertung : Das Produkt verursacht keine Umweltschäden.

##### 12.3. Bioakkumulationspotenzial

Bewertung : Das Produkt verursacht keine Umweltschäden.

##### 12.4. Mobilität im Boden

Bewertung : Das Produkt verursacht keine Umweltschäden.

##### 12.5. Ergebnisse der PBT- und vPvB-Beurteilung

: Nicht als PBT oder vPvB klassifiziert.

##### 12.6. Andere schädliche Wirkungen

Wirkung auf die Ozonschicht	: Keine.
Auswirkung auf die globale Erwärmung	: Keine.

#### ABSCHNITT 13. Hinweise zur Entsorgung

##### 13.1. Verfahren der Abfallbehandlung

: Kann an einem gut gelüfteten Platz in die Atmosphäre abgelassen werden. Nicht in die Kanalisation, Keller, Arbeitsgruben und ähnliche Plätze, an denen die Ansammlung des Gases gefährlich werden könnte, ausströmen lassen. Lieferant nach besonderen Empfehlungen fragen.

Verzeichnis gefährlicher Abfälle (Entscheidung der Kommission EG 2001/118) : 16 05 05: Gase in Druckbehältern andere als unter 16 05 04 genannt.

##### 13.2. Zusätzliche Information

: Keine.

	<b>SICHERHEITSDATENBLATT</b> gemäß RL 1907/2006/EG (REACH)	Seite : 8 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

#### ABSCHNITT 14. Angaben zum Transport

##### 14.1. UN-Nummer

UN-Nummer : 1066

Gefahrzettel Nr. nach ADR/RID,  
Kennzeichnung nach IMDG, IATA



: 2.2 : Nicht entzündbare, nicht giftige Gase.

##### 14.2. Ordnungsgemäße UN-Versandbezeichnung

Transport im Straßen-/ Eisenbahnverkehr (ADR/RID) : STICKSTOFF, VERDICHTET

Transport im Luftverkehr (ICAO-TI / IATA-DGR) : NITROGEN, COMPRESSED

Transport im Seeverkehr (IMDG) : NITROGEN, COMPRESSED

##### 14.3. Transportgefahrenklassen

Transport im Straßen-/ Eisenbahnverkehr (ADR/RID)

Klasse : 2

ADR/RID Klassifizierungscode : 1 A

Nummer zur Kennzeichnung der Gefahr : 20

Tunnel Beschränkungscode : E : Durchfahrt verboten durch Tunnel der Kategorie E.

Transport im Luftverkehr (ICAO-TI / IATA-DGR)

Transport im Seeverkehr (IMDG)

Emergency Schedule (EmS) - Fire : F-C

Emergency Schedule (EmS) - Spillage : S-V

##### 14.4. Verpackungsgruppe

Transport im Straßen-/ Eisenbahnverkehr (ADR/RID) : Nicht anwendbar.

Transport im Luftverkehr (ICAO-TI / IATA-DGR) : Nicht anwendbar.

Transport im Seeverkehr (IMDG) : Nicht anwendbar.

##### 14.5. Umweltgefahren

Transport im Straßen-/ Eisenbahnverkehr (ADR/RID) : Keine.

Transport im Luftverkehr (ICAO-TI / IATA-DGR) : Keine.

Transport im Seeverkehr (IMDG) : No

##### 14.6 Besondere Vorsichtsmaßnahmen für den Verwender

Verpackungsanweisung(en)

Transport im Straßen-/ Eisenbahnverkehr (ADR/RID) : P200

Transport im Luftverkehr (ICAO-TI / IATA-DGR)

Transport im Seeverkehr (IMDG)

	<b>SICHERHEITSDATENBLATT gemäß RL 1907/2006/EG (REACH)</b>	Seite : 9 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

#### ABSCHNITT 14. Angaben zum Transport (Forts.)

Passenger and Cargo Aircraft	: Allowed / Erlaubt.
Packing instruction - Passenger and Cargo Aircraft	: 200
Cargo Aircraft only	: Allowed
Packing instruction / Cargo Aircraft only	: 200
Transport im Seeverkehr (IMDG)	: P200
Besondere Vorsichtsmaßnahmen für den Verwender	: - Ausreichende Lüftung sicherstellen. Der Fahrer muß die möglichen Gefahren der Ladung kennen und er muß wissen, was bei einem Unfall oder Notfall zu tun ist. Vor dem Transport : - Behälter sichern. - Das Flaschenventil muß geschlossen und dicht sein. - Die Ventilverschlußmutter oder der Verschlußstopfen (soweit vorhanden) muß korrekt befestigt sein. - Die Ventilschutzeinrichtung (soweit vorhanden) muß korrekt befestigt sein. Möglichst nicht in Fahrzeugen transportieren, deren Laderaum nicht von der Fahrerkabine getrennt ist.

#### 14.7 Massengutbeförderung gemäß Anhang II des MARPOL-Übereinkommens 73/78 und gemäß IBC-Code

Massengutbeförderung gemäß Anhang II des MARPOL-Übereinkommens 73/78 und gemäß IBC-Code: Not applicable.

#### ABSCHNITT 15. Rechtsvorschriften

##### 15.1. Vorschriften zu Sicherheit, Gesundheits- und Umweltschutz/spezifische Rechtsvorschriften für den Stoff oder das Gemisch

###### EG-Gesetzgebung

Verwendungsbeschränkung(en)	: Keine.
Seveso Richtlinie 96/82/EG	: Nicht angeführt.

###### Nationale Gesetzgebung

	: Alle nationalen/örtlichen Vorschriften beachten.
- 4. BImSchV	
- Wassergefährdungsklasse WGK	: NWG - Nicht wassergefährdend.
- Sonstige Gesetze und Technische Regeln (Nicht vollständig)	: BetriebssicherheitsV mit TRBSen insbesondere TRBS 3145 / TRGS 725 "Ortsbewegliche Druckgasbehälter", TRGS 2141, BGR Regel 500 Teil 2.33: "Umgang mit Gasen", GefahrstoffV mit Technischen Regeln Gefährliche Stoffe TRGS insbesondere TRGS 407 "Tätigkeiten mit Gasen - Gefährdungsbeurteilung", TRGS 400, 500, 510, 900.

##### 15.2. Stoffsicherheitsbeurteilung

: Eine Stoffsicherheitsbeurteilung (CSA) muß für dieses Produkt nicht erstellt werden.

	<b>SICHERHEITSDATENBLATT</b> <b>gemäß RL 1907/2006/EG (REACH)</b>	Seite : 10 / 10
		Versions-Nr. : 3 - 02
		Datum : 4 / 3 / 2015
		Ersetzt : 17 / 8 / 2012
<b>Stickstoff (verdichtet)</b>		<b>089A</b>

<b>ABSCHNITT 16. Sonstige Angaben</b>
---------------------------------------

<b>Änderungen</b>	: Überarbeitetes Sicherheitsdatenblatt in Übereinstimmung mit der Verordnung (EU) Nr. 453/2010.
<b>Schulungshinweise</b>	: Das Risiko des Erstickens wird oft übersehen und muß bei der Unterweisung der Mitarbeiter besonders hervorgehoben werden.
<b>Weitere Angaben</b>	: Dieses Sicherheits-Datenblatt wurde im Einklang mit geltenden europäischen Richtlinien erstellt. Es gilt für alle Länder, die diese Richtlinien in ihre nationale Gesetzgebung übernommen haben.
<b>Volltext der Gefahrenhinweise in Abschnitt 3.</b>	: H280 - Enthält Gas unter Druck; kann bei Erwärmung explodieren.
<b>HAFTUNGSAUSSCHLUSS</b>	: Bevor das Produkt in irgendeinem neuen Prozeß oder Versuch benutzt wird, sollte eine sorgfältige Untersuchung über die Materialverträglichkeit und die Sicherheit durchgeführt werden. Die Angaben in diesem Dokument sind keine vertraglichen Zusicherungen von Produkteigenschaften. Sie stützen sich auf den heutigen Stand der Kenntnisse.

Ende des Dokumentes

# B-2 Potassium Hydroxide solution (KOH) safety data sheet



## SAFETY DATA SHEET

### SECTION 1: PRODUCT AND COMPANY IDENTIFICATION

#### Potassium Hydroxide

**Product Name:** Caustic Potash, Caustic Potash Flake, Caustic Potash Walnut, Caustic Potash 90%, Caustic Potash Briquettes 90%

**Identified Uses:** Chemical manufacturing, fertilizer, batteries, soaps

**Company Information:**

ASHTA Chemicals Inc.

P.O. Box 858

Ashtabula Ohio 44005

**Phone:** (440) 997-5221

**Fax:** (440) 998-0286

**24-hour Emergency Phone:** CHEMTREC: (800) 424-9300

### SECTION 2: HAZARDS IDENTIFICATION

**GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)**

**GHS label elements, including precautionary statements:**

**Signal Word:** Danger

**Pictogram(s):**



<b>Hazard Statements</b>	
H301	Toxic if swallowed.
H314	Causes severe skin burns and eye damage
H318	Causes serious eye damage.
H402	Harmful to aquatic life.
<b>Precautionary Statements</b>	
P260	Do not breathe dust/ fume/ gas/ mist/ vapors/ spray.
P264	Wash skin thoroughly after handling.
P273	Avoid release to the environment.
P270	Do not eat, drink or smoke when using this product.
P280	Wear protective gloves/eye protection/face protection.
P301 + P310	IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.
P301 + P330 + P331	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.



P303 + P361+ P353	IF ON SKIN (or hair): Remove/ Take off immediately all contaminated clothing. Rinse SKIN with water/ shower.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P304 + P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P310	Immediately call a POISON CENTER or doctor/ physician.
P321	Specific treatment (see supplemental first aid instructions on this label).
P390	Absorb spillage to prevent material damage.
P363	Wash contaminated clothing before reuse.
P405	Store locked up.
P406	Store in corrosive resistant stainless steel container with a resistant inner liner.
P501	Dispose of contents/container to an approved waste disposal plant.

**SECTION 3: COMPOSITION/INFORMATION ON INGREDIENTS**

**Synonyms:**

CHEMICAL NAME:	Potassium Hydroxide
TRADE NAME:	Caustic Potash, Caustic Potash Walnut, Anhydrous
SYNONYMS:	Caustic Potash, Potassium Hydrate, Lye, KOH
CONCENTRATION:	>90% potassium hydroxide (balance is moisture)

C.A.S:	1310-58-3
WHMIS:	D1B, E

CHEMICAL FORMULA:	KOH
CHEMICAL FAMILY:	Alkali

**SECTION 4 FIRST AID MEASURES**

**Description of first aid measures:**

Move out of dangerous area. Consult a physician. Show this safety data sheet to the doctor in attendance.

**If inhaled**

If breathed in, move person into fresh air. If breathing is difficult, give humidified air. Give oxygen but only by a certified physician. If breathing stops, provide artificial respiration. Get medical attention immediately.

**In case of skin contact**

Immediately take off all contaminated clothing. Wash off IMMEDIATELY with plenty of water for at least 15-20 minutes. Get medical attention. Wash clothing separately before reuse. Destroy or thoroughly clean contaminated shoes.

**In case of eye contact**

Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Call a physician or poison control center immediately.

**If ingested**

Never give anything by mouth to an unconscious person. Rinse mouth with water. Give plenty of water to drink. Consult a physician.



**SECTION 5 FIRE FIGHTING MEASURES**

Flash Point:	Material is not flammable.
Extinguishing Media:	Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.
Auto Ignition Temp:	Non-combustible.
Special Fire Fighting Procedures:	Wear self-contained breathing apparatus and full protective clothing. In case of fire and/or explosion do not breathe fumes. Move containers from fire area if you can do so without risk. Use water spray to cool unopened containers.
Unusual Fire/Explosion Hazards:	Reacts with metals (aluminum, brass, copper, zinc, etc.) to generate flammable hydrogen gas, which then may cause fire and explosion.

**SECTION 6 ACCIDENTAL RELEASE MEASURES**

**Environmental Precautions:**  
Do not discharge into drains, water courses or onto the ground.

**Containment and Cleaning:**  
Cleanup personnel must wear proper protective equipment. Completely contain spilled material with dikes, sandbags, etc., and prevent any run-off into ground or surface waters or sewers. Recover as much material as possible into containers for disposal. Remaining material may be neutralized with dilute hydrochloric or acetic acid. Neutralization products, both liquid and solid, must be recovered for disposal.

**Waste Control Procedures:**  
All disposals of this material must be done in accordance with federal, state and local regulations. Waste characterization and compliance with disposal regulations are the responsibilities of the waste generator.

**SECTION 7: HANDLING AND STORAGE**

**Precautions to be taken for handling and storage:**  
This material generates considerable amounts of heat when added to water. Storage areas should be free of potential contact with acids, organics and reactive metals. Keep container tightly closed. Store in a cool, dry, well-ventilated place. Store in corrosive resistant container with a resistant inner liner. Store away from incompatible materials. Store at temperatures not exceeding 40°C/104°F. Compatible storage materials may include, but not be limited to, the following: nickel and nickel alloys, steel, plastics, plastic or rubber-lined steel, FRP or Derakane vinyl ester resin.

**Precautions for repair:**  
**Equipment:** Only personnel trained and qualified in handling this product should prepare equipment for maintenance. Wash thoroughly with water.

**Other Precautions:** Spillage, when wet can be slippery. Potassium hydroxide is very hygroscopic and will become wet upon sitting in open moist air.



**SECTION 8: EXPOSURE CONTROL/PERSONAL PROTECTION**

**Principal Component:** Potassium Hydroxide

**Occupational Exposure Limits:**

ACGIH TLV = 2 mg/m<sup>3</sup> (ceiling)

OSHA PEL = None

15 Minute STEL = None

NIOSH IDLH = None

**Exposure Controls:**

Eye Protection: Chemical splash goggles and face shield.

Respiratory Protection: None is normally required, however, if dusting, misting or heavy vapor formation should occur, a NIOSH approved respirator shall be worn.

Other Protection: Rubber boots. Rubbers over leather shoes are not recommended. Rubber apron, rainwear or disposal tyvek suit with hard hat should be worn.

Ventilation Recommended: Provide adequate ventilation to meet TLV requirements.

Glove Type Recommended: Rubber, nitrile, neoprene, PVL.

Additional Information: Safety eyewash/shower stations must be available in the work area.

**Appropriate Engineering Controls:**

Good general ventilation should be used. Ventilation rates should be matched to conditions. If applicable, use process enclosures, local exhaust ventilation, or other engineering controls to maintain airborne levels below recommended exposure limits. If exposure limits have not been established, maintain airborne levels to an acceptable level. Eye wash facilities and emergency shower must be available when handling this product.

**SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES**

Information on basic physical and chemical properties:

Appearance	Whitish flake, walnut, pieces, etc.
Odor	No odor
Odor Threshold	Not available
pH	>14 (in aqueous solution)
Initial boiling point	1,320°C
Flash point	Not flammable
Evaporation rate	No data available
Flammability (solid, gas)	Not flammable
Upper/lower flammability or explosive limits	Not flammable
Autoignition Temperature	No data available
Water solubility	Very soluble
Physical State	Solid at room temperature
Molecular Weight	56.1
Melting Point	361°C
Specific Gravity (water = 1)	2.044 at 15.6°C (60°F)



Bulk Density	1,300 kg/m <sup>3</sup>
Vapor Pressure	No data available
Vapor Density	No data available
Partition Coefficient: n-octanol/water	No data available

<b>SECTION 10:</b>	<b>STABILITY AND REACTIVITY</b>
--------------------	---------------------------------

Stability:	Stable under normal condition.
Conditions to avoid:	Exposure to air can form potassium carbonate.
Incompatibility:	Organic chemicals, nitrocarbons, halocarbons and certain metals or alloys (aluminum, brass, copper, zinc, etc.). Oxidizing agents, acids. Initiates or catalyzes violent reactions of acetaldehyde, acrolein or acrylonitrile.
Hazardous decomposition products:	When KOH and certain metals (aluminum, brass, copper, zinc, etc.) react, hydrogen is generated which can be flammable or explosive.
Polymerization:	Hazardous polymerization will generally not occur.
Additional Information:	Trichlorethylene will react to form dichloroacetylene, which is spontaneously flammable.

<b>SECTION 11:</b>	<b>TOXICOLOGICAL INFORMATION</b>
--------------------	----------------------------------

**Information on likely routes of exposure:**

**Skin Contact:** Major potential hazard - contact with the skin can cause severe burns with deep ulcerations. Contact with solution or mist can cause multiple burns with temporary loss of hair at contact site. Solutions may not cause immediate pain or irritation upon skin contact. Prolonged or repeated contact with dilute solutions may cause drying and cracking of skin and possible skin damage.

**Skin Absorption:** It can penetrate to deeper layers of skin and corrosion will continue until removed. The severity of injury depends on the concentration and the duration of exposure.

**Eye Contact:** Major potential hazard – Liquid in the eye can cause severe destruction and blindness. These effects can occur rapidly affecting all parts of the eye. Mist or dust can cause irritation with high concentrations causing destructive burns.

**Inhalation:** By analogy with sodium hydroxide, inhalation of solution mist is expected to cause mild irritation at 2 mg/m<sup>3</sup>. More severe burns and tissue damage in the upper respiratory tract can occur at higher concentrations. Pneumonitis can result from severe exposures.

**Ingestion:** Ingestion of potassium hydroxide can cause severe burning and pain in lips, mouth, tongue, throat and stomach. Severe scarring of the throat can occur after swallowing. Death can result from ingestion.

**Information on toxicological effects:**

Irritancy:	A study with a 10% solution showed severe tissue damage when applied to skin for 4 hours.
Sensitization:	Not available
Carcinogenicity:	Potassium hydroxide is not listed on the IARC, OSHA or NTP carcinogen lists.
Teratogenicity & Mutagenicity:	Not available
Reproductive Toxicology :	Not available
Toxicological Synergism :	Not available

**Product Species Test Results:**

LD<sub>50</sub>: 333 mg/kg (rat oral)  
LC<sub>50</sub>: Fresh water mosquito fish: 80.0 mg/L (24 Hours, static)

**SECTION 12: ECOLOGICAL INFORMATION****Ecological Information:**

Persistence and degradability:	No data is available on the degradability of this product.
Bioaccumulative potential:	No data available for this product.
Mobility in soil:	Not available.
Other adverse effects:	No other adverse environmental effects (e.g. ozone depletion, photochemical ozone creation potential, endocrine disruption, global warming potential) are expected from this component.
Aquatic Toxicity:	May cause shifts in water pH outside the range of pH 7-9. This change may be toxic to aquatic organisms.

**Biodegradability:**

Not biodegradable (biodegradability term pertains to an organic material capable of decomposition as a result of attack by microorganisms). However, potassium hydroxide will be neutralized by acidity present in natural environment.

**SECTION 13: DISPOSAL CONSIDERATIONS**

Collect and reclaim or dispose in sealed containers at licensed waste disposal site if possible. Do not allow this material to drain into sewers/water supplies. Do not contaminate ponds, waterways or ditches with chemical or used container. Dispose of contents/container in accordance with local/regional/national/international regulations. Empty containers or liners may retain some product residues.

**SECTION 14: TRANSPORT INFORMATION****Shipping:**

Usual Shipping Containers:	Tank car, Tank truck, ABS Drums.
Usual Shelf Life:	Sealed containers, unlimited.
Storage/Transport Temperatures:	Ambient.

**Suitable Storage:**

Materials/Coatings: Steel, plastic, polyethylene (when dry).



Unsuitable: Aluminum or galvanized containers.

**D.O.T. Information:**

UN number: 1813

Class: 8

Packing group: II

Proper shipping name: Potassium Hydroxide, solid

Reportable Quantity (RQ): 1000 lbs (100% KOH basis)

Marine pollutant: No

Poison Inhalation Hazard: No

**SECTION 15 REGULATORY INFORMATION**

**SARA 302 Components**

SARA 302: Not listed.

**SARA 313 Components**

SARA 313: Not regulated.

**SARA 311/312 Hazards**

Acute health hazard.

**Massachusetts Right To Know Components**

Potassium Hydroxide CAS#: 1310-58-3

**Pennsylvania Right To Know Components**

Water CAS#: 7732-18-5

Potassium Hydroxide CAS#: 1310-58-3

**New Jersey Right To Know Components**

Water CAS#: 7732-18-5

Potassium Hydroxide CAS#: 1310-58-3

**California Prop. 65 Components**

This product does not contain any chemicals known to state of California to cause cancer, birth defects, or any other reproductive harm.

OSHA PSM TPQ: Not listed

**Toxic Substances Control Act (TSCA):**

CAS# 1310-58-3 is listed on the TSCA inventory.

**Comprehensive Environmental Response Compensation Liability Act: (CERCLA)**

CAS# 1310-58-3 is listed on the CERCLA list.

**SECTION 16 OTHER INFORMATION**



**NFPA Rating:**  
Health Hazard: 3  
Fire Hazard: 0  
Reactivity Hazard: 1

**HMIS Rating:**  
Health Hazard: 3  
Chronic Health Hazard:  
Flammability: 0  
Physical Hazard: 1

This information is drawn from recognized sources believed to be reliable. ASHTA Chemicals, Inc. Makes no guarantees or assumes any liability in connection with this information. The user should be aware of changing technology, research, regulations, and analytical procedures that may require changes herein. The above data is supplied upon the condition that persons will evaluate this information and then determine its suitability for their use. Only U.S.A regulations apply to the above.

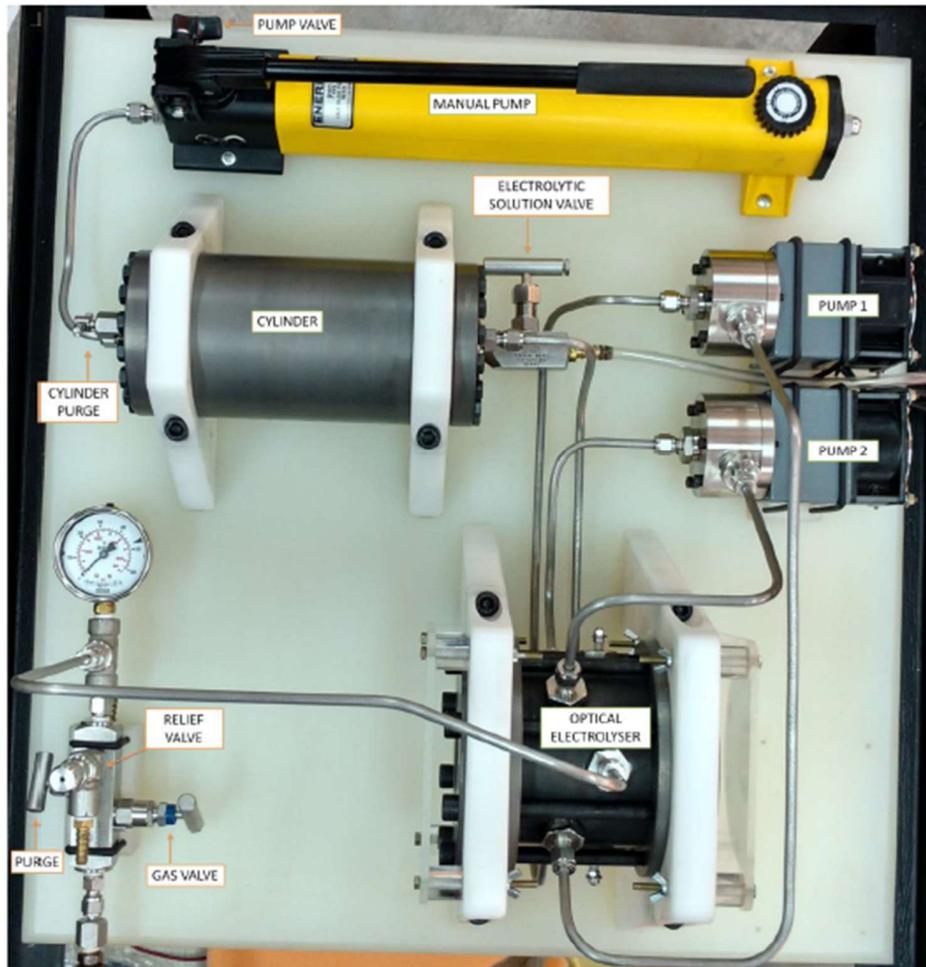
Version 1.0	For the new GHS SDS Standard	Revision Date: 2/4/2015
Version 1.1	Graphics updated	Revision Date: 3/9/2015
Version 1.2	Description update	Revision Date: 4/20/2015
Version 1.3	Changes to Sections 1, 9	Revision Date: 7/29/2015

## B-3 Electrolyzer.

Mechanical Engineering Department–Energy Area



### High Pressure Optical Electrolyser STANDARD OPERACION PROCEDURE



#### Device Description:

The 8 port optical cylinder allows electric and hydraulic connections. Connectors are provided to meet the different requirements.

The tank configuration 1 components are two caps with glass viewers together with the set of M10x150 bolts and the 210 bar relief valve. This configuration must be used with pressures of up to 200 bar.

The tank configuration 2 components are two caps with glass viewers together with the set of M12x150 bolts and the 500 bar relief valve. This configuration must be used with pressures of up to 450 bar. When this configuration is adopted, the recirculation pumps must not be connected.

#### Tank Configuration changing procedure:

Make sure that the chamber is empty, without pressure (see D1/D2) and that the electrodes are unplugged. Remove the safety acrylic glass and disconnect all the tube-connectors and the electrode wires. Loosen the tank bolts (without taking them out) before loosening the frame bolts.

Remove the upper frame of the supporting structure and take the tank into a safe and clean table. With the bolts heads facing the roof, loosen them and take them out. Change carefully the caps, making sure that all the bolts are tightened in small adjusting steps one bolt after the other until the metal contact between the cylinder and the caps is sure. Put the tank again into the frame and place the tubing connectors or caps in the tank. **Make sure that the pumps are not linked to the tank if the configuration 2 is adopted.**

Once the tank and the tubing are placed, tighten the frame. Finally, change the relief valve according to the configuration used.

#### A. Required protection equipment.

- Ocular protection during experimentation is required.
- Use gloves and overall for handling the electrolytic solution.

#### B. Required special supplies.

- 1- Electrolytic solution.
- 2- Nitrogen tank.
- 3- 900 cm<sup>3</sup> of hydraulic oil.

#### C. System pressurization

- 1- Charge pump with 900 cm<sup>3</sup> of hydraulic oil.
- 2- Retraction of piston: Verify that the purge valve, the electrolytic solution valve and the gas valve are closed and that the pump valve is open. Next open the nitrogen tank tap, previously connected, and control the flow of gas, using the gas valve, until the flow stops, ensuring a complete retraction of the piston. Finally close the gas valve and release the chamber pressure using the purge valve; close the purge valve.
- 3- Electrolytic solution fill: Open the electrolytic solution valve and pour the required amount of solution using a funnel (see the annexed table); close the valve.
- 4- Open the gas valve until the required initial pressure is reached; close the valve and the nitrogen tank tap.
- 5- Close the pump valve and make sure that the pump cap is in venting position. Finally pump until the required pressure is reached.

#### D1. System depressurization (electrolytic solution volume unchanged)

- 1- Open the pump valve partially until the pressure of the hydraulic oil is relieved (avoid opening abruptly), close the pump valve.
- 2- Open the purge valve until the pressure of the chamber is completely relieved (according to the manometer lecture); close the purge valve.

#### D2. Despresurization with electrolytic solution emptying.

- 1- Open the pump valve partially until the pressure of the hydraulic oil is relieved (avoid opening abruptly), close the pump valve.
- 2- Open the purge valve until a pressure of 10 to 20 bar is reached; close the purge valve.
- 3- Carefully open the electrolytic solution valve to empty the required amount of electrolytic solution (do not open the valve abruptly to avoid splatter of the solution); close valve.

## **Appendix C**

### Experiments Description of High Pressure Electrolyzer



# C-1 Description of experiments

## Introduction

The experiments aim to give experimental support to simulation data. Water electrolysis under high pressure is performed to supply information about the behavior of hydrogen bubbles. The optical chamber is filled up with KOH solution and nitrogen. The alkaline solution is the electrolyte needed for the electrolysis, while nitrogen pressurizes the chamber and generates a free surface with the KOH. Optical measurements are taken with a camera and a laser. Electrodes and power supply are also used in these experiments.

## Experiments

Electrolysis is performed at different pressures and is rise up to 200bar. Optical measurements are taken, analyzing this data:

- Bubble detachment diameter and bubble rising velocity.
- Production of single bubbles.
- Interaction between the free surface and the bubble diameter.

The following devices are used for the experiments:

- High-pressure electrolyzer.
- Electrical source: Function generator and oscilloscope.
- Laser: Double-pulsing-Nd:YAG.
- Camera: CCD-Camera. Resolution of 1280 x 1024 Pixel.
- Microscope.
- Computer: Core II Duo, 2 Ghz, 3 GB RAM.

Electrolyzer is filled up with KOH solution and pressurized with nitrogen.

Electrical source is turned to start the electrolysis.

For the optical measurements, the laser is used on one window to ensure that the observation field bubbles are all illuminated in the same way. A diffusor is attached in order to get this homogeneous illumination. For the experiments the position of the focal point can be adjusted. On the other window of the electrolyzer the camera is installed for capturing the images. A long distance microscope is placed ahead of the camera, in order to achieve a high depth of sharpness in the observation window. The computer is connected to the system in order to control the trigger of the laser and to capture the data of the camera. It is intentioned to take 50 pictures in each round of measurement.

## **C-2 Checklist for the experiments in HPE at KIT**

### **Preparation**

- Electrolyzer prepared and ready to use.
- Check all safety measures.
- Exhaust and drain mechanism are prepared.
- To turn on the laser, follow the laser manual.
- Check if data acquisition, laser and video camera are working.
- Set the data acquisition and video camera to standby.
- Pressurize the electrolyzer and fill it with KOH solution.
- Switch on the electrical source in order to start the electrolysis
- Start data collection procedure.

### **Experiment**

- Follow the experimental plan.
- Check voltage and current, optical measurements and data collection.
- Check the time needed for the experiment and H<sub>2</sub> production.

### **Follow-up:**

- Save the test data.
- Inspection of HPE.
- Depressurize and drain KOH solution.
- To turn off the laser, follow the laser manual.
- Close valves and turn off the power supply.

# D

## KOH Solution Safety Data Sheet





P303 + P361+ P353	IF ON SKIN (or hair): Remove/ Take off immediately all contaminated clothing. Rinse SKIN with water/ shower.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P304 + P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P310	Immediately call a POISON CENTER or doctor/ physician.
P321	Specific treatment (see supplemental first aid instructions on this label).
P390	Absorb spillage to prevent material damage.
P363	Wash contaminated clothing before reuse.
P405	Store locked up.
P406	Store in corrosive resistant stainless steel container with a resistant inner liner.
P501	Dispose of contents/container to an approved waste disposal plant.

**SECTION 3: COMPOSITION/INFORMATION ON INGREDIENTS**

**Synonyms:**

CHEMICAL NAME:	Potassium Hydroxide
TRADE NAME:	Caustic Potash, Caustic Potash Walnut, Anhydrous
SYNONYMS:	Caustic Potash, Potassium Hydrate, Lye, KOH
CONCENTRATION:	>90% potassium hydroxide (balance is moisture)

C.A.S:	1310-58-3
WHMIS:	D1B, E

CHEMICAL FORMULA:	KOH
CHEMICAL FAMILY:	Alkali

**SECTION 4 FIRST AID MEASURES**

**Description of first aid measures:**

Move out of dangerous area. Consult a physician. Show this safety data sheet to the doctor in attendance.

**If inhaled**

If breathed in, move person into fresh air. If breathing is difficult, give humidified air. Give oxygen but only by a certified physician. If breathing stops, provide artificial respiration. Get medical attention immediately.

**In case of skin contact**

Immediately take off all contaminated clothing. Wash off IMMEDIATELY with plenty of water for at least 15-20 minutes. Get medical attention. Wash clothing separately before reuse. Destroy or thoroughly clean contaminated shoes.

**In case of eye contact**

Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Call a physician or poison control center immediately.

**If ingested**

Never give anything by mouth to an unconscious person. Rinse mouth with water. Give plenty of water to drink. Consult a physician.



**SECTION 5 FIRE FIGHTING MEASURES**

Flash Point:	Material is not flammable.
Extinguishing Media:	Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.
Auto Ignition Temp:	Non-combustible.
Special Fire Fighting Procedures:	Wear self-contained breathing apparatus and full protective clothing. In case of fire and/or explosion do not breathe fumes. Move containers from fire area if you can do so without risk. Use water spray to cool unopened containers.
Unusual Fire/Explosion Hazards:	Reacts with metals (aluminum, brass, copper, zinc, etc.) to generate flammable hydrogen gas, which then may cause fire and explosion.

**SECTION 6 ACCIDENTAL RELEASE MEASURES**

**Environmental Precautions:**  
Do not discharge into drains, water courses or onto the ground.

**Containment and Cleaning:**  
Cleanup personnel must wear proper protective equipment. Completely contain spilled material with dikes, sandbags, etc., and prevent any run-off into ground or surface waters or sewers. Recover as much material as possible into containers for disposal. Remaining material may be neutralized with dilute hydrochloric or acetic acid. Neutralization products, both liquid and solid, must be recovered for disposal.

**Waste Control Procedures:**  
All disposals of this material must be done in accordance with federal, state and local regulations. Waste characterization and compliance with disposal regulations are the responsibilities of the waste generator.

**SECTION 7: HANDLING AND STORAGE**

**Precautions to be taken for handling and storage:**  
This material generates considerable amounts of heat when added to water. Storage areas should be free of potential contact with acids, organics and reactive metals. Keep container tightly closed. Store in a cool, dry, well-ventilated place. Store in corrosive resistant container with a resistant inner liner. Store away from incompatible materials. Store at temperatures not exceeding 40°C/104°F. Compatible storage materials may include, but not be limited to, the following: nickel and nickel alloys, steel, plastics, plastic or rubber-lined steel, FRP or Derakane vinyl ester resin.

**Precautions for repair:**  
**Equipment:** Only personnel trained and qualified in handling this product should prepare equipment for maintenance. Wash thoroughly with water.

**Other Precautions:** Spillage, when wet can be slippery. Potassium hydroxide is very hygroscopic and will become wet upon sitting in open moist air.



**SECTION 8: EXPOSURE CONTROL/PERSONAL PROTECTION**

**Principal Component:** Potassium Hydroxide

**Occupational Exposure Limits:**

ACGIH TLV = 2 mg/m<sup>3</sup> (ceiling)

OSHA PEL = None

15 Minute STEL = None

NIOSH IDLH = None

**Exposure Controls:**

Eye Protection: Chemical splash goggles and face shield.

Respiratory Protection: None is normally required, however, if dusting, misting or heavy vapor formation should occur, a NIOSH approved respirator shall be worn.

Other Protection: Rubber boots. Rubbers over leather shoes are not recommended. Rubber apron, rainwear or disposal tyvek suit with hard hat should be worn.

Ventilation Recommended: Provide adequate ventilation to meet TLV requirements.

Glove Type Recommended: Rubber, nitrile, neoprene, PVL.

Additional Information: Safety eyewash/shower stations must be available in the work area.

**Appropriate Engineering Controls:**

Good general ventilation should be used. Ventilation rates should be matched to conditions. If applicable, use process enclosures, local exhaust ventilation, or other engineering controls to maintain airborne levels below recommended exposure limits. If exposure limits have not been established, maintain airborne levels to an acceptable level. Eye wash facilities and emergency shower must be available when handling this product.

**SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES**

Information on basic physical and chemical properties:

Appearance	Whitish flake, walnut, pieces, etc.
Odor	No odor
Odor Threshold	Not available
pH	>14 (in aqueous solution)
Initial boiling point	1,320°C
Flash point	Not flammable
Evaporation rate	No data available
Flammability (solid, gas)	Not flammable
Upper/lower flammability or explosive limits	Not flammable
Autoignition Temperature	No data available
Water solubility	Very soluble
Physical State	Solid at room temperature
Molecular Weight	56.1
Melting Point	361°C
Specific Gravity (water = 1)	2.044 at 15.6°C (60°F)



Bulk Density	1,300 kg/m <sup>3</sup>
Vapor Pressure	No data available
Vapor Density	No data available
Partition Coefficient: n-octanol/water	No data available

<b>SECTION 10:</b>	<b>STABILITY AND REACTIVITY</b>
--------------------	---------------------------------

Stability:	Stable under normal condition.
Conditions to avoid:	Exposure to air can form potassium carbonate.
Incompatibility:	Organic chemicals, nitrocarbons, halocarbons and certain metals or alloys (aluminum, brass, copper, zinc, etc.). Oxidizing agents, acids. Initiates or catalyzes violent reactions of acetaldehyde, acrolein or acrylonitrile.
Hazardous decomposition products:	When KOH and certain metals (aluminum, brass, copper, zinc, etc.) react, hydrogen is generated which can be flammable or explosive.
Polymerization:	Hazardous polymerization will generally not occur.
Additional Information:	Trichlorethylene will react to form dichloroacetylene, which is spontaneously flammable.

<b>SECTION 11:</b>	<b>TOXICOLOGICAL INFORMATION</b>
--------------------	----------------------------------

**Information on likely routes of exposure:**

**Skin Contact:** Major potential hazard - contact with the skin can cause severe burns with deep ulcerations. Contact with solution or mist can cause multiple burns with temporary loss of hair at contact site. Solutions may not cause immediate pain or irritation upon skin contact. Prolonged or repeated contact with dilute solutions may cause drying and cracking of skin and possible skin damage.

**Skin Absorption:** It can penetrate to deeper layers of skin and corrosion will continue until removed. The severity of injury depends on the concentration and the duration of exposure.

**Eye Contact:** Major potential hazard – Liquid in the eye can cause severe destruction and blindness. These effects can occur rapidly affecting all parts of the eye. Mist or dust can cause irritation with high concentrations causing destructive burns.

**Inhalation:** By analogy with sodium hydroxide, inhalation of solution mist is expected to cause mild irritation at 2 mg/m<sup>3</sup>. More severe burns and tissue damage in the upper respiratory tract can occur at higher concentrations. Pneumonitis can result from severe exposures.

**Ingestion:** Ingestion of potassium hydroxide can cause severe burning and pain in lips, mouth, tongue, throat and stomach. Severe scarring of the throat can occur after swallowing. Death can result from ingestion.



**Information on toxicological effects:**

Irritancy:	A study with a 10% solution showed severe tissue damage when applied to skin for 4 hours.
Sensitization:	Not available
Carcinogenicity:	Potassium hydroxide is not listed on the IARC, OSHA or NTP carcinogen lists.
Teratogenicity & Mutagenicity:	Not available
Reproductive Toxicology :	Not available
Toxicological Synergism :	Not available

**Product Species Test Results:**

LD<sub>50</sub>: 333 mg/kg (rat oral)  
LC<sub>50</sub>: Fresh water mosquito fish: 80.0 mg/L (24 Hours, static)

**SECTION 12: ECOLOGICAL INFORMATION**

**Ecological Information:**

Persistence and degradability:	No data is available on the degradability of this product.
Bioaccumulative potential:	No data available for this product.
Mobility in soil:	Not available.
Other adverse effects:	No other adverse environmental effects (e.g. ozone depletion, photochemical ozone creation potential, endocrine disruption, global warming potential) are expected from this component.
Aquatic Toxicity:	May cause shifts in water pH outside the range of pH 7-9. This change may be toxic to aquatic organisms.

**Biodegradability:**

Not biodegradable (biodegradability term pertains to an organic material capable of decomposition as a result of attack by microorganisms). However, potassium hydroxide will be neutralized by acidity present in natural environment.

**SECTION 13: DISPOSAL CONSIDERATIONS**

Collect and reclaim or dispose in sealed containers at licensed waste disposal site if possible. Do not allow this material to drain into sewers/water supplies. Do not contaminate ponds, waterways or ditches with chemical or used container. Dispose of contents/container in accordance with local/regional/national/international regulations. Empty containers or liners may retain some product residues.

**SECTION 14: TRANSPORT INFORMATION**

**Shipping:**

Usual Shipping Containers:	Tank car, Tank truck, ABS Drums.
Usual Shelf Life:	Sealed containers, unlimited.
Storage/Transport Temperatures:	Ambient.

**Suitable Storage:**

Materials/Coatings: Steel, plastic, polyethylene (when dry).



Unsuitable: Aluminum or galvanized containers.

**D.O.T. Information:**

UN number: 1813

Class: 8

Packing group: II

Proper shipping name: Potassium Hydroxide, solid

Reportable Quantity (RQ): 1000 lbs (100% KOH basis)

Marine pollutant: No

Poison Inhalation Hazard: No

**SECTION 15 REGULATORY INFORMATION**

**SARA 302 Components**

SARA 302: Not listed.

**SARA 313 Components**

SARA 313: Not regulated.

**SARA 311/312 Hazards**

Acute health hazard.

**Massachusetts Right To Know Components**

Potassium Hydroxide CAS#: 1310-58-3

**Pennsylvania Right To Know Components**

Water CAS#: 7732-18-5

Potassium Hydroxide CAS#: 1310-58-3

**New Jersey Right To Know Components**

Water CAS#: 7732-18-5

Potassium Hydroxide CAS#: 1310-58-3

**California Prop. 65 Components**

This product does not contain any chemicals known to state of California to cause cancer, birth defects, or any other reproductive harm.

OSHA PSM TPQ: Not listed

**Toxic Substances Control Act (TSCA):**

CAS# 1310-58-3 is listed on the TSCA inventory.

**Comprehensive Environmental Response Compensation Liability Act: (CERCLA)**

CAS# 1310-58-3 is listed on the CERCLA list.

**SECTION 16 OTHER INFORMATION**



**NFPA Rating:**  
Health Hazard: 3  
Fire Hazard: 0  
Reactivity Hazard: 1

**HMIS Rating:**  
Health Hazard: 3  
Chronic Health Hazard:  
Flammability: 0  
Physical Hazard: 1

This information is drawn from recognized sources believed to be reliable. ASHTA Chemicals, Inc. Makes no guarantees or assumes any liability in connection with this information. The user should be aware of changing technology, research, regulations, and analytical procedures that may require changes herein. The above data is supplied upon the condition that persons will evaluate this information and then determine its suitability for their use. Only U.S.A regulations apply to the above.

Version 1.0	For the new GHS SDS Standard	Revision Date: 2/4/2015
Version 1.1	Graphics updated	Revision Date: 3/9/2015
Version 1.2	Description update	Revision Date: 4/20/2015
Version 1.3	Changes to Sections 1, 9	Revision Date: 7/29/2015



# E

## Maintenance and Cleaning



## A. Objective:

Clarified the maintenance work and modifications that were applied to the experimental high-pressure electrolyzer.

## B. Scope:

Regarding the experiments that were done, and thinking about future operations, maintenance and modifications were planned.

## C. Cleaning and Maintenance

It has been noticed, that remains of electrolyte have solidified at the electrolyzer surface. White powder was found over the exterior surface, mainly on one of the ports where the electrodes are fixed and on the solution valve.

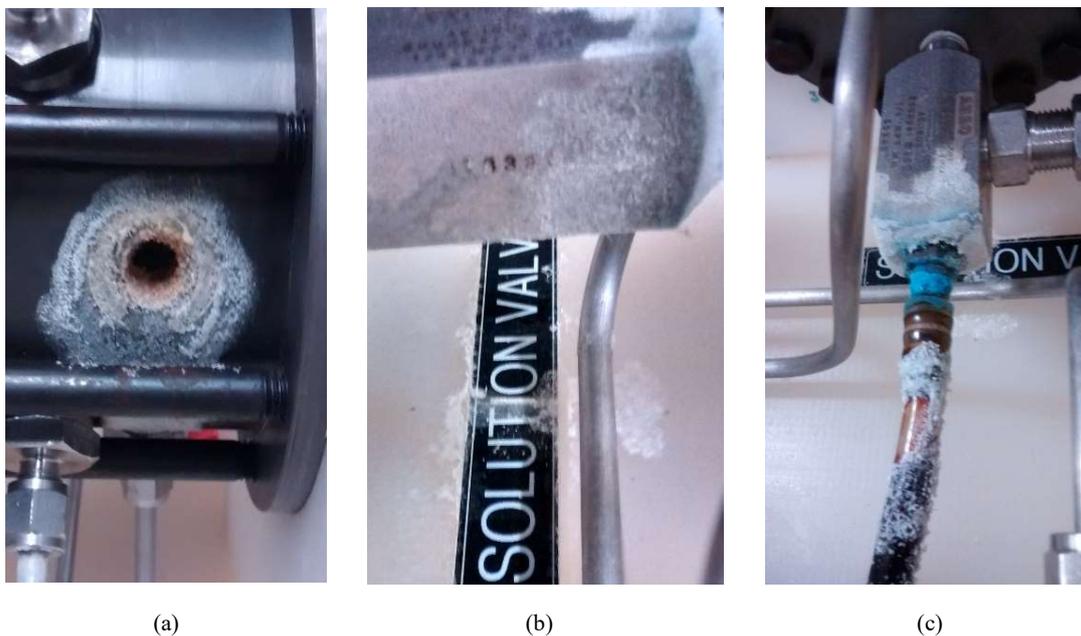


Figure E 1: Electrolyzer surface. (a) Hole for electrode. (b),(c) Solution Valve.

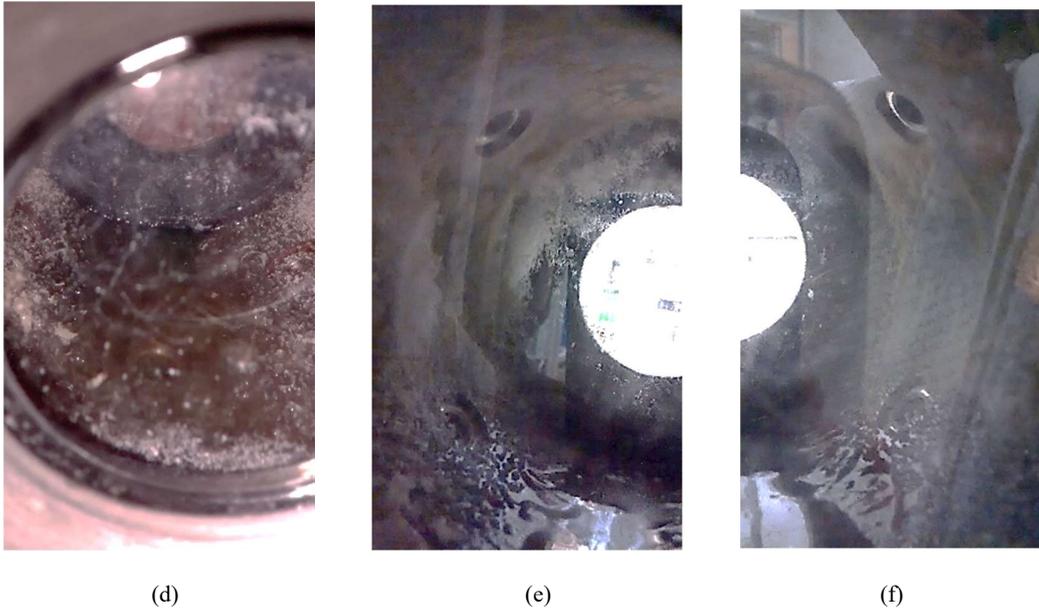


Figure E 2: Electrolyzer optical chamber. (d) lens. (e), (f) interior of chamber.

## C.1 Cleaning

A series of instructions are suggested in order to make a cleaning of the exterior and interior of the equipment.

### Outside cleaning:

- I. With dry brush, if possible hard bristle, remove the external incrustations at the chamber and tank.
- II. With the dry brush, clean the dirty connections leading to the vessel.
- III. Finish cleaning with a brush and enough water.

### Inside cleaning:

- I. Place the electrodes or the plugs in order to seal that the chamber.
- II. Connect a clean water supply to the gas inlet supply. Water should be still. Circulate water by means of a centrifugal pump. Close the bleed valve and keep gas valves and electrolyte solution open.
- III. Circulate water intensively through the equipment. Drain the water that leaves the hose through the solution valve into a recipient. Insist on this procedure until it is observed through the lenses that the incrustations and leftovers have been removed.
- IV. While circulating water through the equipment, activate recirculation pumps. Control is done by visual inspections.

## C.2 Modification

In this section modifications are proposed, as was mention security and safety were the main focus, also operation of the equipment was taken into account.

### a. Container

It was decided to place the electrolyzer inside a container made out of metal sheets and a metal tub. The purpose is to contain the electrolyte solution in case of leakage and provide mechanical protection in case of a failure while working at high pressure. The container should permit operation of the equipment (valves and manual pump), and give access to lenses for the camera and laser in order to take optical measurements.

Figure R.3 shows the final disposition of the equipment inside the container. Each metal sheets in front the camera and laser have an orifice, which permits the laser and camera to go inside the container in order to take optical measurements.



Figure E 3: Set-up with container

Drawing can be found in appendix B. This work was it done at the institute's workshop.

### b. Feeding vale

Originally, the feeding valve was installed without any separator from the electrolyzer, what represented a risk for the operator when experiments were performed at high pressure. In order to minimize this risk, valves were placed outside the container. The connection between the valves and the electrolyzer was done with a stainless still tube. Figure E.4 shows this modification.



Figure E 4: Optical chamber, pressure valves and gauge – New connection.

### c. Exhaust valve

A plastic tube was added to the exit of the exhaust valve. The main reason is to maintain certain distance between the exhaust gases and the operator. KOH solution droplets may be contained in the exhaust gases. The exit of the plastic tube was introduced in a plastic can, which afterwards needs to be delivered to final deposition.

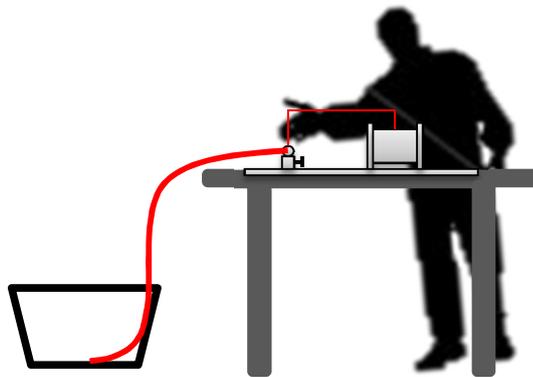


Figure E 5: Exhaust plastic tube scheme

# F

## Hydrogen Production



## A. H<sub>2</sub> LFL in air 4% vol. - 1 bar:

First approach hypothesis:

- 1) Atmospheric pressure.
- 2) Gas volume inside vessel: 0.2 liters. Nitrogen volume is considered as air.
- 3) H<sub>2</sub> Lower Flammability limit: 4% nitrogen, accompanied with 2% O<sub>2</sub>
- 4) Continues constant current is applied.
- 5) 4 – 4.5 kWh/Nm<sup>3</sup>H<sub>2</sub> efficiency of the electrolysis. 2 mA and 2V.
- 6) Electrode of 0.05mm. Active surface is only their cross section.

The supplied power is calculated and so the amount of hydrogen production per time. This amount has to be always under the 4% vol. in air. As the energy consumption is given in moles, the LFL of hydrogen in vol. % was converted into mole quantities.

Table F.1: Energy consumption and electrical source values.

ITBA - KIT Electrolyzer		
Generation Factor (kWh/Nm <sup>3</sup> )	4	4.5
Temperature	Ambient Temp.	
Voltage (V)	1.5	2
Current density (kA/cm <sup>2</sup> )	5.09E-02	1.02E-01
Power (kW)	1.70E-03	4.00E-03

Table F.1 shows the power input of the electrolyzer, then the production of hydrogen is:

Table F.2: Hydrogen generation per hour.

Generation x h	1.00E-06	Nm <sup>3</sup>
	1.00E-03	N Liters
	9.00E-08	kg
	4.46E-05	Moles

Finally, comparing this result with the limit of hydrogen production, results that electrolysis can be hold during approximately 8 hours, giving enough time to perform a complete round of experiments.

Table F.3: Operation Hours at atmospheric pressure.

moles H <sub>2</sub> limit	3.57E-04
moles H <sub>2</sub> x hour ITBA-KIT Electrolyzer	4.46E-05
Operation hours	8.00

The calculation was done for atmospheric pressure, since hydrogen presents its widest flammability limits at this pressure. This statement is supported by YU. N. SHEBEKO's observation [20], which show the narrowing of the hydrogen flammability limit with increasing pressures. Schroeder also confirms this fact [21]. Figure F.1 shows the narrowing of the flammability limits.

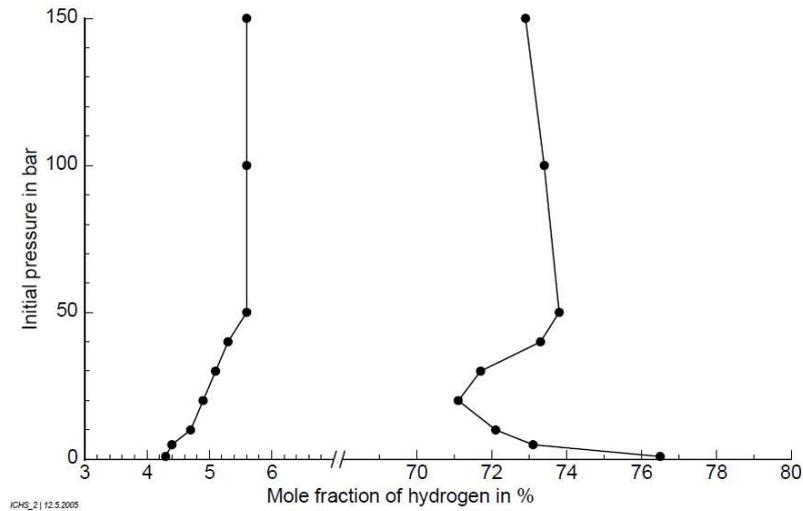


Figure F.1: Influence of the initial pressure on the explosion limits of hydrogen-air mixtures, measured at room temperature. Schroeder, 2003. [21]

## B. H<sub>2</sub> LFL in N<sub>2</sub> and O<sub>2</sub> - 1 bar

In this case, hydrogen production is simulated over time. Due to hydrogen and oxygen generation, pressure inside the vessel increase, this also was calculated.

Second approach hypothesis:

- 1) Atmospheric pressure.
- 2) Gas volume inside vessel: 0.2 liters of Nitrogen at  $t = 0$ .
- 3) LFL of 4% vol. used as limit.
- 4) Direct constant current is applied.
- 5) 1 – 2 mA, and voltage, 1.5 – 2 V.
- 6) Electrode of 0.05mm. Active surface is only their cross section.

Table F.4 shows the time in seconds, the volume in liters of each gas and there percentage in the mixture.

Table F.4: H<sub>2</sub> and O<sub>2</sub> volume production and vol. % in mixture.

T	N2 vol (L)	H2 vol (L)	O2 vol (L)	TOTAL	N2 vol %	H2 vol %	O2 vol %
33600	2.00E-01	8.49E-03	4.24E-03	2.13E-01	94.01%	3.99%	1.99%
33700	2.00E-01	8.52E-03	4.25E-03	2.13E-01	94.00%	4.00%	2.00%
33800	2.00E-01	8.54E-03	4.27E-03	2.13E-01	93.98%	4.01%	2.00%

The partial pressure of each component and the total pressure of the vessel is also calculated. At the moment where the LFL is reached, the total pressure inside the cylinder is 1.07 bar.

Table F.5: Partial pressures of  $H_2$ ,  $N_2$  and  $O_2$  in the mixture at the time were 4% vol. of  $H_2$  is been reached in mixture.

P. Press N2	P. Press H2	P. Press O2	Ptotal
1.00E+00	4.62E-02	2.41E-02	1.07E+00
1.00E+00	4.63E-02	2.41E-02	1.07E+00
1.00E+00	4.64E-02	2.42E-02	1.07E+00

Table F.6: Operation time needed to reach 4% vol. of  $H_2$  in mixture.

Operation Time (h)	9.41
--------------------	------

As it can be seen in table F.6 electrolysis can be run approx. nine and half hours until the LFL is reached.

### 5.4.3 High pressure

Experiments are pretended to be performed at 200bar. This calculation shows, which is the time limit before the relief valve is activated. In this case 210bar are needed to be reached inside the vessel. Pressure increases due to the production of hydrogen and oxygen. For higher pressures Z factor was introduced, equation 5.1 was used:

$$p = \frac{Z\bar{R}T}{v} \quad (5.1)$$

Table F.7: Partial pressures of  $H_2$ ,  $N_2$  and  $O_2$  in the mixture at the time were total pressure of 210bar is reached.

T (s)	P. Press N2	P. Press H2	P. Press O2	Ptotal
4.42E+06	201.09	6.19	2.72	210.00

Table F.8: Operation time in hours were the total pressure of the mixture is 210 bar.

Operation Time (h)	1227
--------------------	------

1227 hours are needed to reach 210 bar.

For both calculations a direct constant current was supposed. However, instead of D.C. as power supply, the experiments are being performed using a square shape signal with periods between 210ms and 710ms and pulse time between 10ms and 100ms. This reduces the generation of hydrogen in comparison to the D.C. signal, giving the possibility of extending the operation time.

Operation time here calculated is longer than in previous works [4], due to the pulsed signal and also because a smaller current value was used. For the current experiments, the maximum current is approx. to 2mA in comparison to 200mA that were used before.



# G

## Measurement List



Bubble Size - Rising Velocity							
Hydrogen				Oxygen			
Pressure [bar]	Voltage [V]	Time Pulse [ms]	Period [ms]	Pressure	Voltage [V]	Time Pulse [ms]	Period [ms]
1	1.5	50	450	1bar	1.5	50	450
	1.6	10	510		1.6	10	510
	1.7	10	210		1.7	10	210
	1.8	10	510		1.8	10	510
	1.9	10	710		1.9	10	710
20	1.7	10	1010	20	1.7	10	1010
	1.9	10	710		1.9	10	710
40	1.7	10	1010	40	1.7	10	1010
	1.9	10	710		1.9	10	710
60	1.7	10	1010	60	1.7	-	-
	1.9	10	710		1.9	10	710
80	1.7	10	1000	80	1.7	10	1000
	1.9	10	710		1.9	10	710
140	1.7	-	-	140	1.7	-	-
	1.9	-	-		1.9	-	-
180	1.7	10	1010	180	1.7	-	-
	1.9	10	710		1.9	-	-

Lifetime at Free Surface				
Gas	Pressure [bar]	Voltage [V]	Time Pulse [ms]	Period [ms]
Hydrogen	1	1.9	15	2010
Hydrogen	1	2	-	-
Oxygen	1	2	-	-

